

METALLURGIA

THE BRITISH JOURNAL OF METALS

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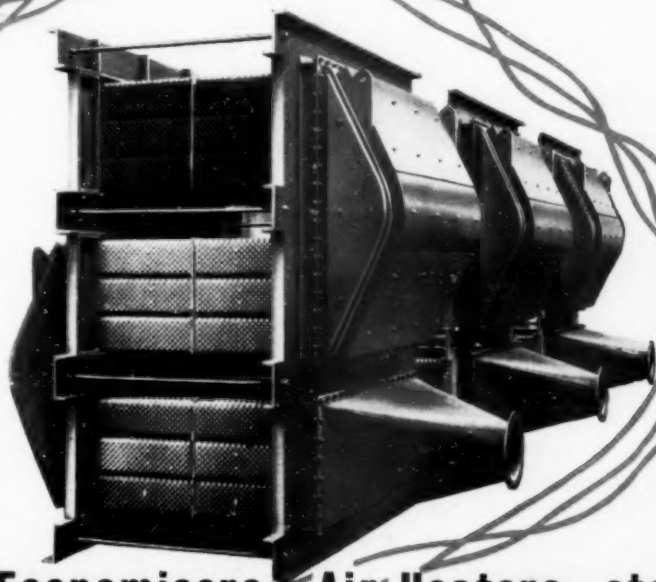
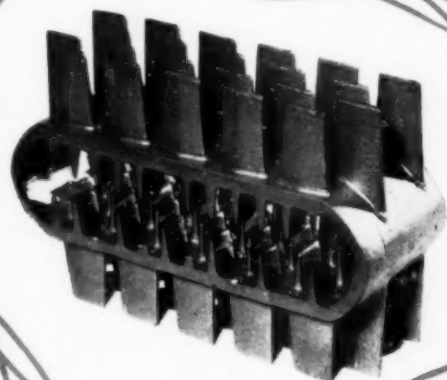
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METALLURGIA

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INCORPORATING THE METALLURGICAL ENGINEER

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METALLURGIA

THE BRITISH JOURNAL OF METALS

INCORPORATING THE "METALLURGICAL ENGINEER"

JANUARY, 1956

Vol. LII. No. 315

Steel Supplies

THE steel industry has enjoyed a decade of expansion since the end of the war: in ten years output has increased by two-thirds. A substantial proportion of existing capacity is completely new and much of the remainder has been modernised. Output per furnace of both pig iron and steel is 75% higher than ten years ago, the total steel output having averaged an annual increase of 5½%—from under 12 million tons in 1945 to nearly 20 million tons last year. In parallel with this increase in production, new and modernised plants have helped the industry to use raw materials with ever-increasing efficiency and economy, as instanced by the fact that fuel consumption per ton of steel has been cut by about 15% since the end of the war. Output of alloy steels needed for high quality and precision engineering has more than doubled. In 1946, the first full peace-time year, output was 535,000 tons as against an estimated output of 1,200,000 tons in 1955.

In 1955 the total supply of steel in this country was 21·7 million ingot tons, of which imports contributed 8½%. This total supply was 2·2 million tons more than in 1954: supplies to British industry were raised by 1·8 million ingot tons and exports by 0·4 million. Home production of steel in 1955 is estimated at nearly 19·8 million tons, an increase of more than 1½ million tons on 1954, when 18·52 million tons were produced. This year it is hoped to achieve a further increase of more than 6% to bring 1956 production to a new high record of 21 million tons of steel and 13,800,000 tons of pig iron.

In spite of this picture of steadily growing production there is still a shortage of steel, for 1955 was a year in which the demand for steel outstripped the capacity of British steelmakers to supply it, with the result that imports were higher than in any year since 1952. Similar conditions of strain, of steel production up to capacity, of full order books, and of lengthening delivery periods prevailed in the steelmaking countries of the continent. In a letter to the *Financial Times*, Mr. H. N. Edwards, Managing Director of Metropolitan-Carriage and Wagon Co., Ltd., suggests that customers must feel confused by the complicated situation which exists. On the one hand they read of record steel outputs, and on the other they are being told that deliveries of finished products are being delayed by the lack of it. Mr. Edwards continues . . . "It is not enough to say that a certain firm received x tons of steel in a given year, if that tonnage excludes vital sections without which the vehicles cannot be completed." In the shipyards, too, steel shortages are causing difficulties. Although the supply of plates has improved, sections now appear to be the "nigger in the woodpile." When any large quantity of steel sections is required in an overhaul, it is the practice in at least one yard to have the ship in for measuring, and then to allow

it to continue in service until the consignment arrives and the repairs can be done.

One of the factors responsible for the present unsatisfactory position is that the aggregate increase in steel consumption in this country during the past two years has been of the order of 15%—an unprecedented rate of expansion—and, although the output of ingots last year was 1½ million tons above the 1954 level, this increase was not enough. It is evident, from the experience of the last two years, that over a given period the steel-using industries can expand their consumption of steel much faster than the steel industry can expand its production. This is due to the much greater volume of investment per unit of output required in the steel industry, and the longer time which must elapse before that investment yields its fruit. The necessity of relatively greater investment is equally true of the raw material producing industries in relation to the steel industry—the opening of a new ore-field is a longer business even than the establishment of a new steel plant. Nor are raw material supplies the only limitations facing the industry: there is also the factor of port and transport facilities. Even if the plant capacity had been available, it would not have been possible in the circumstances of 1955 to have brought into Great Britain the requisite additional supplies of imported ore and coal to allow of the expansion of ingot production by, say, 1 million tons.

There is thus in the nature of things an upper limit against which any sharp expansion in the use of steel must eventually strike. The most the steel industry can do in the circumstances is to try to gauge as realistically as it can the limitations by which it is itself confronted and, having regard to them, to endeavour to accommodate as even a rate of growth in the use of steel as is possible.

An average rate of increase of 4½% a year in the use of steel has been registered between 1948 and 1955. If this rate of growth continues, and if allowance is made for a small increase in direct exports, a steel requirement of some 24 million ingot tons is indicated for 1958, and of some 28 million ingot tons for 1962. The practicability of meeting this latter requirement is, at the present time, the subject of a close investigation, in the course of which many problems will have to be considered.

In the first place, there is the problem of space, and although the need for opening up fresh sites seems to be indicated now, the production cost per ton will be considerably greater on a green site than on an extended existing site. Raw materials, too, are an important factor, particularly as the necessity for underground mining of home ore looms ahead, and competition for the available world ore supplies increases. Furthermore, future supplies of coking coal remain one of the industry's greatest uncertainties. Finally, there is the question of

Continued on page 49

Meeting Diary

24th January

Institute of British Foundrymen (Coventry Section). "Developments in Mould and Core Making Processes," by A. TIPPER. Coventry Technical College, Room A.5. 7.30 p.m.

25th January

Institute of British Foundrymen (Birmingham Branch). "The Metallurgy of Cast Iron," by H. MORROGH. James Watt Memorial Institute, Great Charles Street, Birmingham, 3. 7.15 p.m.

Institution of Engineering Inspection (West of Scotland Branch). "Use of Electro Deposits and Ancillary Processes in the Protection of Metals," by S. A. J. MURRAY. St. Enoch Hotel, Glasgow. 7.30 p.m.

Society of Chemical Industry (Corrosion Group). "Prevention of Corrosion in the Heavy Chemical Industry," by F. R. HIMSWORTH and W. D. CLARK. Joint Meeting with the Chemical Engineering Group. King's College, Strand, London, W.C.2. 6.30 p.m.

Society of Instrument Technology (South Wales Section). "Photo-Electric Cells and their Application," by L. BATTYL. Physics Lecture Theatre, Cardiff College of Technology. 6.45 p.m.

26th January

Incorporated Plant Engineers (Merseyside and North Wales Branch). "Some Aspects of Heat Transfer," by C. S. PARRY. Grosvenor Hotel, Chester. 7.15 p.m.

Institute of British Foundrymen (Northampton Section). "Master Pattern Making Aids Production," by H. WILSON. Hind Hotel, Wellingborough. 7.30 p.m.

Institute of Fuel (East Midland Section). "Recent Developments in Fuel Technology," by PROF. A. L. ROBERTS. Gas Showrooms Lecture Theatre, Nottingham. 6.15 p.m.

Institute of Fuel (Midland Section). "The Occurrence, Extraction and Properties of Germanium," by A. R. POWELL. James Watt Institute, Great Charles Street, Birmingham, 3. 6 p.m.

Institute of Metals (Birmingham Local Section). "Electrolytic and Chemical Methods of Brightening," by H. SILMAN. Birmingham Exchange and Engineering Centre, Stephenson Place, Birmingham. 6.30 p.m.

27th January

Institute of British Foundrymen (Falkirk Section). "Further Thoughts on Cupola Practice," by W. Y. BUCHANAN. Temperance Cafe, Lint Riggs, Falkirk. 7.30 p.m.

North East Coast Institution of Engineers and Shipbuilders. "Nuclear Reactors for the Generation of Power," by C. E. ILIFFE. Mining Institute, Newcastle upon Tyne. 6.15 p.m.

28th January

Society of Leather Trades' Chemists, Ltd. "Metal Sequestration," by B. HUGHES, together with a paper to be given by DR. P. DANBY. Reynolds Hall, College of Technology, Manchester. 2 p.m.

31st January

Sheffield Metallurgical Association. "Inspection and Testing of High Quality Steel Castings," by J. JOHNSON. B.I.S.R.A. Laboratories, Hoyle Street, Sheffield, 3. 7 p.m.

Society of Chemical Industry (Corrosion Group). "La Cooperation Technique Européenne," by J. GERARD. S.C.I. Jubilee Memorial Lecture—Joint Meeting with London Section. Royal Institution, Albemarle Street, London, W.1. 6 p.m.

Society of Instrument Technology. "Industrial Measurement of Gas Temperature," by A. M. GOODRIDGE, DR. R. JACKSON and G. G. THURLOW. Manson House, 26, Portland Place, London, W.1. 6.30 p.m. for 7 p.m.

1st February

Institute of Fuel. "The Harnessing of Nuclear Power for Industry," by J. L. GILLAMS. Institution of Civil Engineers, Great George Street, London, S.W.1. 5.30 p.m.

Institution of Engineering Inspection (Birmingham Branch). "Shell Moulding," by M. C. DIXON. Birmingham Exchange and Engineering Centre, Birmingham. 7.30 p.m.

Manchester Metallurgical Society. "Cast Iron," by I. C. H. HUGHES. Manchester Room, Central Library, Manchester. 6.30 p.m.

2nd February

Institute of Metals (Birmingham Local Section). "Modern Case-Hardening Processes," by P. F. HANCOCK. James Watt Memorial Institute, Great Charles Street, Birmingham. 6.30 p.m.

Institute of Metals (London Local Section). "Thermit Processes," by T. BURCHELL. 4, Grosvenor Gardens, London, S.W.1. 6.30 p.m.

Leeds Metallurgical Society. "Metallurgy in Relation to Gas-Turbines," by DR. J. M. ROBERTSON. Large Chemistry Lecture Theatre, The University, Leeds, 2. 7.15 p.m.

3rd February

Institute of Fuel (South Wales Section). "Research at the National Coal Board," by DR. W. IDRIS JONES, C.B.E. South Wales Institute of Engineers, Park Place, Cardiff. 6 p.m.

7th February

Incorporated Plant Engineers (London Branch). "Electronics in Industry," by J. E. FIELDEN. Royal Society of Arts, John Adam Street, Adelphi, London, W.C.2. 7 p.m. (preceded by tea at 6.30 p.m.).

Institute of Metals (Oxford Local Section). Junior Members' Evening. Discussion on "Purification." (1) Zone Refining of Metals; (2) Vacuum Distillation of Metals; (3) Properties of Super-Purity Aluminium. Ballroom of the Cadena Cafe, Cornmarket Street, Oxford. 7 p.m.

Institute of Metals (South Wales Local Section). "Shell Moulding," by M. C. DIXON. Department of Metallurgy, University College, Singleton Park, Swansea. 6.45 p.m.

Sheffield Metallurgical Association. "Chromatographic Methods of Inorganic Analysis," by A. A. NORTH. B.I.S.R.A. Laboratories, Hoyle Street, Sheffield, 3. 7 p.m.

8th February

Institute of Fuel (North-Western Section). "Some Recent Advances in Fuel Research," by DR. W. IDRIS JONES, C.B.E. Joint Meeting with the National Smoke Abatement Society, North Western Division. Engineers' Club, Albert Square, Manchester. 2.30 p.m. Members' Luncheon at 1 p.m.

Institution of Engineering Inspection. "Isotopes in Industry," by J. C. ROCKLEY. Royal Society of Arts, John Adam Street, Adelphi, London, W.C.1. 6.45 p.m.

9th February

Incorporated Plant Engineers (Glasgow Branch). "Engineering Metals," by J. WINNING. Scottish Building Centre, 425-427, Sauchiehall Street, Glasgow. 7 p.m.

Institute of Welding (South London Branch). "Welding Metallurgy and Electrode Development," by J. MERCER. 2, Savoy Hill, London, W.C.2. 6 p.m. for 6.30 p.m.

Liverpool Metallurgical Society. "Radiation Damage to Metals," by DR. W. M. LOMER. Liverpool Engineering Society, 9, The Temple, Dale Street, Liverpool. 7 p.m.

13th February

Institute of Metals (Scottish Local Section). "Titanium," by J. W. RODGERS. Institution of Engineers and Shipbuilders in Scotland, 39, Elmbank Crescent, Glasgow, C.2. 6.30 p.m.

North East Metallurgical Society. "An Outline of the Modern Metallurgy of Cast Iron," by H. MORROGH. Cleveland Scientific and Technical Institution, Middlesbrough. 7.15 p.m.

14th February

Incorporated Plant Engineers (Manchester Branch). "Application of Maintenance of Centrifugal Pumps," by G. O. STEVENSON and A. J. CLEMENTS. Engineers Club, Albert Square, Manchester. 7.15 p.m.

Institute of Welding (Slough Section). "The Part of Resistance Welding in Automation," by R. W. AYERS. Lecture Room, Community Centre, Farnham Road, Slough, Bucks. 7 p.m. for 7.30 p.m.

Institution of Engineering Inspection (Leeds Branch). "Recent Developments in Metrology with Special Reference to Interferometry," by W. FOSTER. Theological Library, Leeds Church Institute, Albion Place, Leeds, 1. 7.30 p.m.

Institution of Engineering Inspection (South-Western Branch). "The Manufacture and Uses of Tufnol," by Chief Inspector, Tufnol, Birmingham. Grand Hotel, Broad Street, Bristol. 7.30 p.m.

Sheffield Metallurgical Association. "Research and Development on Continuous Casting of Steel," by J. SAVAGE. B.I.S.R.A. Laboratories, Hoyle Street, Sheffield, 3. 7 p.m.

The Electrodeposition of Tungsten

By G. L. Davis, Ph.D., B.Sc., A.R.I.C., F.I.M.

and C. H. R. Gentry, B.Sc., F.R.I.C.

Material Research Laboratory, Mullard, Ltd., Mitcham

More advantage could be taken of the refractory properties of metals such as tungsten, molybdenum, zirconium and tantalum, if they could be applied to other metals as surface coatings. In the present article the authors discuss the electrodeposition of tungsten. No success has been achieved with aqueous baths or with those based on organic solvents. Thick coherent layers of pure tungsten have, however, been deposited from fused salt baths containing borates and tungstic oxide. The main practical objection to the method is the reactivity of the melt, which may introduce difficulties in obtaining suitable containing vessels. The theoretical aspects of electrodeposition from the fused salt baths are treated rather extensively, in the belief that such baths must, in the future, become of increasing importance for the electrowinning and electroplating of many of the refractory metals.

THE refractory metals—tungsten, molybdenum, zirconium, tantalum, etc.—have many unusual and attractive physical or chemical properties, but their use is frequently limited by the difficulty of fabricating them into any but the simplest forms. This disadvantage could often be overcome by applying the metals as surface coatings, and this fact has led to numerous investigations endeavouring to deposit them on steel and other basis metals by various techniques—electrodeposition, cementation, thermal decomposition of volatile halides, thermal decomposition of carbonyls, hydrogen reduction of halides, etc. While some measure of success has been attained with certain of these methods, none has been entirely satisfactory. For this reason, a systematic study of these previous processes was undertaken, and this has led to the development of certain modified or new processes.

The techniques studied have been bounded by the following considerations:—

- (a) The deposited coating, if a pure metal, should have a melting point above $2,000^{\circ}\text{C}$.; if an alloy, it should have its solidus temperature above this value. It should also possess good hot strength, adequate ductility, and reasonable chemical inertness, and should be capable of being deposited with little restriction on its thickness.
- (b) The coating should have good adherence to a cheap basis metal, either directly or after simple preparation.
- (c) The process should be efficient, not too expensive and not so difficult of application that it could not be used on larger than laboratory scale.

It was decided that tungsten was the most promising of the refractory metals, and, consequently, most attention was paid to it. The present paper describes some of the laboratory experiments on one phase of the programme—the electrodeposition of this metal and its alloys.

There is an extensive literature on the electrodeposition of tungsten and its alloys, but it may be emphasised here that this literature contains numerous claims for successful methods which cannot be substantiated.

From aqueous baths, deposits of pure tungsten have been reported on mercury cathodes^{1,2}, on copper cathodes from a tungstate solution^{3,4}, from a saturated sodium carbonate solution with additions of tungsten

trioxide⁵, from a sodium phosphate solution containing tungsten trioxide^{6,7}, and from pertungstate solutions^{8,9}. Many authors have described methods of plating alloys of tungsten, usually with iron, nickel or cobalt. When deposits have been obtained from acid baths, they have been unsatisfactory¹⁰, but from alkaline baths good deposits have been obtained by a number of workers (see especially ¹⁰⁻¹²) although the deposits do not fulfil the requirements set out above.

As early as 1888, it was claimed that tungsten could be electrodeposited from solutions of lithium paratungstate in a number of organic solvents¹³. More recently, thin deposits have been obtained from solutions of tungsten hexachloride in pyridine¹⁴, acetone¹⁵, and glycerol¹⁶. Other workers, however, have reported no electrodeposition of tungsten from solutions of its compounds in organic solvents, although the reduction to a lower valency state has frequently been observed¹⁷.

Fused salt baths, as media from which to plate tungsten, were used by a number of early workers (see review by Smithells¹⁸). The first—and perhaps the only—deposits of any coherence reported in the literature are those stemming from van Liempt baths of fused simple tungstates¹⁹⁻²¹. However, these deposits are always associated with coatings of tungsten bronzes which place some limitation on the thickness of tungsten that can be deposited in one operation. Other workers have been concerned with the electrowinning of tungsten rather than its electroplating, and they have usually obtained powdery deposits, frequently contaminated with compounds such as borides, etc. Baths have included fused phosphates²²⁻²⁶, chlorides²⁷⁻³⁰, and borates³¹⁻³⁴.

For ease of presentation, the experimental work is conveniently grouped under three headings:—

- (a) Deposition from aqueous solutions.
- (b) Deposition from organic solvents.
- (c) Deposition from fused salt baths.

DEPOSITION FROM AQUEOUS SOLUTIONS

Results

Tungsten

The experiments carried out will not be described in detail, since none gave deposits of any practical value. Solutions were prepared from the purest available chemicals, and the compositions of the baths were controlled by accurate weighing out or by analysis. For

cathodes, copper, platinum or steel was used after cleaning by conventional methods. Where published electrolytes were tested, the best conditions suggested by the previous workers were used: in other experiments a given bath was usually tried both at room temperature and hot (e. 80° C.), and with both low and high current densities.

The following baths containing hexavalent tungsten gave either no deposit at all or thin, poorly-adherent, dark deposits, the thickness of which did not increase on continued electrolysis:—

- (a) An acid fluoride bath containing hydrochloric acid and sodium tungstate³⁵.
- (b) Alkaline or ammoniacal tungstate solutions³.
- (c) A saturated sodium carbonate solution containing dissolved tungsten trioxide⁵.
- (d) Solutions of sodium tungstate with ethylene diamine and sufficient sodium hydroxide to bring the pH into the range 11–12.
- (e) An alkaline tungstate solution containing dextrose³⁶.
- (f) A sodium phosphate solution containing dissolved tungsten trioxide^{7, 37}.
- (g) A sodium tungstate solution containing sodium hypophosphate and acetate.
- (h) An alkaline tungstate bath containing citrate and sulphate, operated at boiling point and very high current density.
- (i) An alkaline tungstate bath containing tartrate and ammonium chloride.
- (j) Tungstate baths containing boric acid (with and without the addition of glycerol) made acid, neutral, or alkaline.

Where deposits were obtained from these baths, they were frequently too thin for quantitative analysis: the presence of tungsten in the deposits could be confirmed, but insufficient sample was sometimes available for even a complete qualitative examination. In several cases, however, it was established that significant amounts of iron were present: this and other evidence indicated that the deposits were of iron-tungsten alloys, whose deposition ceased when the traces of iron in the solution had been almost entirely plated out.

Some trials were made of solutions containing lower valency states of tungsten. These solutions were prepared by reduction of the tungsten at a mercury cathode, preliminary polarographic experiments being used to establish the required applied e.m.f. Thus, electrolysis of a solution of sodium tungstate in 11N hydrochloric acid, with a potential on the mercury pool of –0.9 volts versus the saturated calomel electrode, gave an orange red solution of trivalent tungsten. Attempts to deposit directly from this solution were unsuccessful, as also were the attempts using solutions of trivalent tungsten in strongly alkaline cyanide. Further work was carried out with solutions containing lower valency states of tungsten, obtained by electrolysis at the mercury cathode of a solution of sodium tungstate in 7M phosphoric acid. In no case, however, could a deposit be obtained on electrolysis of these reduced solutions.

Following the literature^{8, 9}, attempts were made to plate tungsten from acid solutions containing the per-tungstic acids. A typical solution contained 150 ml. 1:4 sulphuric acid, 100 ml. 5% sodium tungstate solution, and 40 ml. 20 vol. hydrogen peroxide. From this solution, by electrolysis at 10 amp./sq. dm. on to a copper cathode, a black deposit was obtained, which

dissolved on stopping the current. A series of experiments was made with this type of solution, adjusted to various acidities. At pH values of 5.2 and 6.4 the cathodes were merely tarnished, but at pH 3.5 very small deposits were obtained over a range of current densities and temperatures. At pH 1.1, using a platinum anode and a copper cathode, fairly thick black deposits were obtained over a range of conditions. The best deposits were obtained at 50° C. and a current density of 5 amp./sq. dm. X-ray examination showed the deposits to be amorphous, and they were believed to be a mixture of the lower oxides of tungsten, possibly containing some metal.

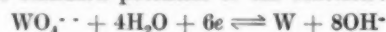
Several attempts were made to co-deposit tungsten with another metal which could subsequently be removed by volatilisation. Experiments were made with various standard mercury or lead electroplating baths with additions of sodium tungstate, but in no case did the deposit contain any detectable amounts of tungsten.

Tungsten Alloys

Alloys of tungsten with the ferrous metals have been obtained by previous investigators from a number of baths. These baths were studied in the present work with the object of so modifying the conditions that the tungsten content of the alloy plate could be substantially increased. Best results have been obtained with ammoniacal citrate baths of the type used by Brenner *et al*¹⁰. By, for example, increasing the ratio of tungsten to ferrous metal and by increasing the current density, higher tungsten contents have, indeed, been obtained. However, the highest that could be reached in mechanically satisfactory deposits was 69% in an iron-tungsten alloy, and 62% in a cobalt-tungsten alloy. Although these deposits were of good appearance and had good adhesion, the tungsten content was not sufficiently high to give them the desired refractory properties. No significant differences were found in the alloys obtained in a limited series of experiments using periodic reverse plating.

Theoretical Considerations

Despite the considerable amount of experimental work, no useful deposit of tungsten has been obtained from aqueous solutions. In fact, it seems very doubtful whether any pure deposit of tungsten has ever been obtained, despite several claims in the literature for very thin plates. These deposits were probably alloys formed from traces of impurity—especially iron—in the solutions used. In the present authors' view it is not, in fact, possible to plate pure tungsten from aqueous baths. It is the reversible electrode potential of a metal which is decisive in the possibility of discharge of its ion at a cathode, although other factors such as concentration over-potential, metal over-potential and hydrogen over-potential may have an influence. This electrode potential represents the difference in free energy of the ions in the solution and the metal in the solid state. Unfortunately, sufficient data are not available to enable this free energy difference to be calculated accurately. Latimer³⁸ has given an approximate value of –1.1 volts for the reversible standard potential of the reaction:—



Since, however, the tungstate ion is prone to the formation of complexes with acid radicles, and its exact form is frequently a function of pH, even this approximate value is not of much significance.

Stackelberg *et al*³⁹ have shown that an alkali metal tungstate, when reduced at the dropping mercury electrode, does not produce a wave in neutral or alkaline solution. In other words, in the "ideal" plating conditions obtaining at a mercury surface, it is easier to deposit the alkali metals than tungsten from solutions of the aquo-tungstate complexes. Tungsten has been reduced at the dropping mercury electrode⁴⁰, to the trivalent state in strong hydrochloric acid solution but, as the applied e.m.f. is raised, hydrogen is discharged before any further reduction to the metal can take place.

From the polarographic evidence, therefore, it would seem that the reversible electrode potential of tungsten has a large negative value, even in simple tungstate solutions. In other solutions, in which the tungsten is present as more stable complexes, even more negative values of the electrode potential are to be expected. It is thus unnecessary to assume a significant metal overvoltage at a tungsten electrode to explain why tungsten cannot be electrodeposited. Even from solutions with a low hydrogen-ion concentration, i.e., alkaline solutions, hydrogen will always be deposited in preference to tungsten. If an attempt is made to reach the tungsten deposition potential by increasing the applied e.m.f., then concentration polarisation or the formation of a gas film will prevent it.

Although it is strongly believed that pure tungsten cannot be electrodeposited from aqueous solutions, tungsten alloys can be plated, and it is pertinent to enquire why this should be so. To reach an understanding of the mechanism of tungsten alloy deposition, the following experimental facts require explanations:—

- (a) The only alloys that have been obtained, in any substantial thickness, are those with iron, nickel and cobalt. (Alloys of manganese and copper with small amounts of tungsten have been claimed, and the deposition of tungsten-chromium alloys at very high current densities has been confirmed by the authors. However, in the latter case only thin deposits can be prepared).
- (b) The deposition of these alloys takes place with high cathode efficiency.
- (c) The composition of the alloys obtained is governed by the pH and composition of the bath. Thus, the type of organic acid and the ratio of ferrous metal to tungstate are critical factors in fixing the composition of the deposit. It is worth noting that either ferrous or ferric iron may be used in these baths.
- (d) There appears to be an upper limit to the tungsten content of the deposits. From Brenner-type baths this was, in the present work, 69% for the iron alloy. No alteration of current density, composition, or other factors will significantly increase these limits.
- (e) The deposits are solid solutions, although according to equilibrium diagrams a fair proportion of an intermetallic compound should be present as another phase. Under the microscope, some of the deposits show a laminated structure, with layers parallel to the basis metal surface.

Several efforts^{41, 42} have been made to explain tungsten-alloy plating, but these are all open to serious criticism. We believe that a useful approach is to start from an examination of the product obtained. This is not only a solid solution, but the linear expansion of the

ferrous metal lattice is 20% smaller than would be expected if the physical properties of the solid solution were additive⁴³. This suggests a large free energy change in the formation of the solid solution, and thus a high affinity of the ferrous metal for tungsten. It is this high affinity which is believed to be largely responsible for the lowering of the deposition potential of the alloy to the point where it occurs in preference to alternative processes such as the deposition of hydrogen.

That the cathode potential required for the deposition of tungsten alloys is very much lower than the estimated deposition potential of tungsten itself is known from the measurements of Holt and Vaaler⁴¹ and of Offermanns and Stackelberg⁴². The latter workers deposited tungsten alloys from a bath containing sodium tungstate, sodium tartrate, sodium sulphate, and iron, nickel or cobalt sulphates, adjusted to pH 7. Under these conditions the deposition potential of the pure nickel from a tungsten-free bath was considerably more negative than that of the nickel-tungsten alloy, a difference of 300 mV. persisting over a wide range of current densities. Brenner *et al*¹⁰ also say that from citrate solution . . . "cobalt and tungsten must have deposition potentials that are close together, otherwise it would be difficult to explain why there is so little variation in the composition of the deposit with current density." It would seem, therefore, that in these baths the deposition potential of the alloys, in the peculiar conditions in which they deposit, is of the same order as, and sometimes less than, the deposition potentials of the individual ferrous metals.

To account for the large free energy change, it may be significant that the alloys of the ferrous metals with tungsten all show extensive solid solution in the ferrous metal region, as well as the formation of intermetallic compounds. It would be not unreasonable to assume that some other metal with similar alloying properties might, therefore, be capable of co-deposition with tungsten. If the phase diagram were favourable, there would be a possibility of obtaining a deposit with properties closer to those required.

DEPOSITION FROM ORGANIC SOLVENTS

The literature on the electrolysis of salts dissolved in organic solvents is, as compared with that available on aqueous bath electrolysis, very sparse. Little fundamental work has been reported, most investigators being concerned with practical attempts to deposit those metals which cannot be satisfactorily plated from aqueous baths. Essential information, e.g., deposition potentials, and even the solubility of the inorganic salts in the organic solvents, is rarely available. This explains the empirical approach which has had perforce to be adopted in the present work.

The general experimental technique was to dissolve tungsten hexachloride and any other solid reagents in the dried solvent maintained under an atmosphere of dried nitrogen. Where necessary the solvent was previously redistilled. Either a 4% solution or, if this could not be prepared, a saturated solution of tungsten hexachloride was used. Electrodeposition was attempted at room temperature (unless otherwise stated), using a copper cathode and a tungsten anode, and applying an e.m.f. of up to 18 volts. The cathode current density was frequently limited by the poor conductance of the solution; it ranged from 0.1 to 20 amp./sq. dm.

The following solvents were used (where mixtures are indicated they contained equal volumes of the two

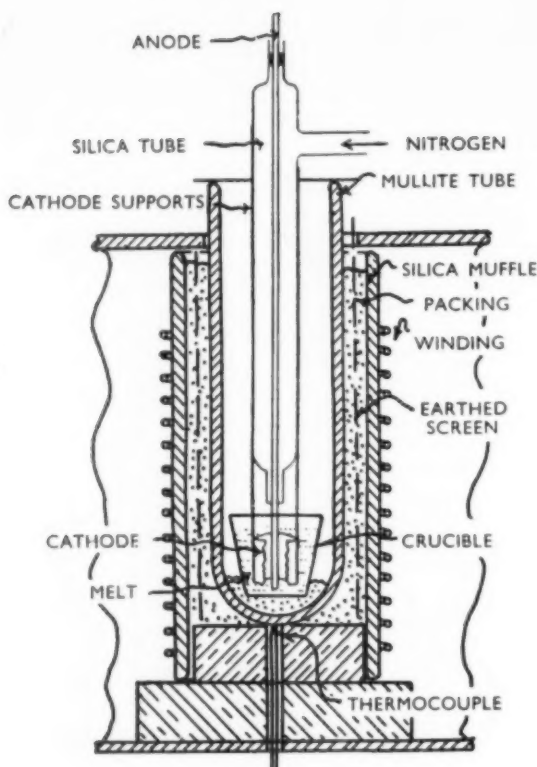


Fig. 1.—Plating assembly.

solvents): acetic acid, acetone, acetonitrile, butyl alcohol, benzene-ethyl bromide, dioxane, dioxane-ethylene glycol (operated at various temperatures up to 90°C.), ethanalamine, ethylene glycol (operated at various temperatures up to 150°C., with and without additions of potassium carbonate), formamide, glycerol, methyl alcohol, nitrobenzene, nitromethane, pyridine-methyl alcohol, triethanolamine, triethanolamine-ethylene glycol, triethanolamine-methyl alcohol. From none of these solvents was a deposit of tungsten obtained.

A similar series of experiments was carried out with solutions of anhydrous sodium tungstate. In most of these solvents, the sodium tungstate was practically insoluble; from the few in which a solution could be obtained, no deposit was visible after electrolysis.

DEPOSITION FROM FUSED SALT BATHS

There are basically two methods of attacking the problem of the electrodeposition of tungsten from fused salt baths: from a compound with the metal held in anion groups (e.g., as tungstates, simple or complexed), or from a tungsten salt. Both have been explored by previous workers.

Van Liempt¹⁹⁻²¹ used simple alkali metal tungstates, and—since the separate salts have high melting points—favoured the use of suitable mixtures fusing at 400–500°C. Even so, the actual electrolysis was carried out some 500°C. above the fusion ranges, in order to take advantage of lowered resistivity and to limit the formation of tungsten bronzes.

Hartmann and co-workers²²⁻²⁴ developed processes for electrowinning of tungsten powder from alkali metal phosphates carrying additions of tungstic oxide. This

approach was refined and extended by Fink and Ma^{25, 26}.

The fusibility of borates—excellent solvents for tungstates and oxides of tungsten—has suggested their suitability as media. Thus, Andrieux²² obtained tungsten as pure metal and combined as borides from fused borates containing oxides of tungsten and zinc.

The choice of baths containing tungsten held as cation is restricted by the instability and volatility of most of the salts of the metal. Some claims have been made, however, for baths of alkali metal salts to which tungsten has been added as chloride^{28, 29}, oxide²⁷ and sulphide³⁰.

As a preliminary to the present work, all the reported baths were examined in some detail over a range of conditions. The results are given in the next section, limitations of space necessitating a brief statement of conclusions only.

On the basis of this examination of reported work, borate baths were selected for further, more detailed, study. This, in turn, led to the formulation of a preferred melt giving much better results than any bath previously proposed. A thorough investigation will be reported of the operating conditions of this preferred melt, and of the examination that was made of the deposits obtained from it.

While the primary aim of the present work was essentially practical, it was thought advisable to obtain some understanding of the fundamental mechanism of the plating process. A limited experimental programme was accordingly carried out, and this has been applied in the theoretical discussion of the behaviour of these fused salt baths.

Experimental

The elevated temperatures and the reactivity of the melts and vapours resulting from them have together caused difficulties in the choice of materials for constructing apparatus. Many ceramic refractories have been tested—silica, alumina, magnesia, spinel, carbon, zirconia—but all have been attacked relatively rapidly. Of the metals, the noble precious metals have been resistant to a useful degree, while pure nickel has proved the most valuable of the baser metals.

Protection from attack on the melts, leads, supports, and, indeed, the deposit itself, has enforced the use of protective atmospheres and, for this purpose, purified nitrogen has been used throughout the work. For most



Fig. 2.—Tungsten from phosphate bath. $\times 1200$

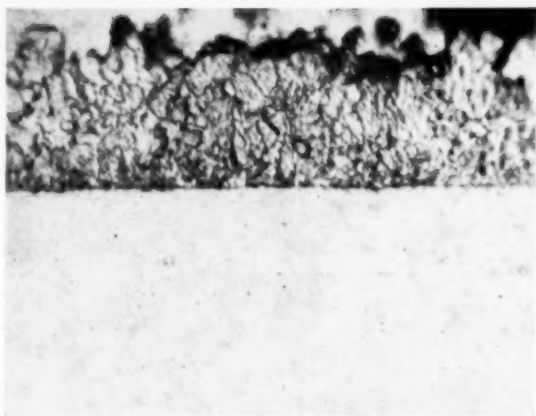


Fig. 3.—Deposit from melt $4\text{Li}_2\text{B}_2\text{O}_4 : 4\text{K}_2\text{B}_2\text{O}_4 : 1\text{WO}_3$,
× 600

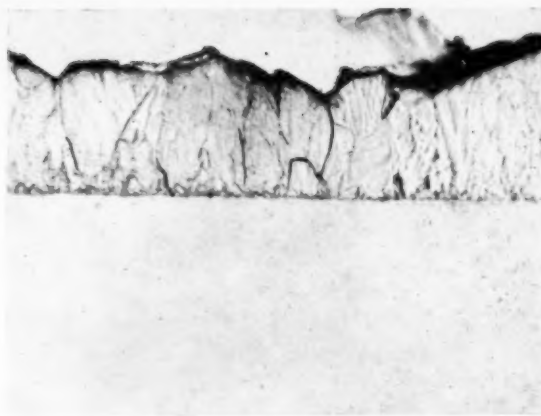


Fig. 4.—Deposit from melt $4\text{Li}_2\text{B}_2\text{O}_4 : 4\text{K}_2\text{B}_2\text{O}_4 : 2\text{WO}_3$,
× 600

melts, platinum was satisfactorily used for the cell vessel: anodes were normally of pure tungsten rod, and cathodes were of platinum or nickel which had been degreased, hydrogen-stoved and then vacuum-stoved to avoid blistering of deposits by gas evolution at the bath-operating temperature.

Baths were made from reagents of AnalaR quality, and (after the importance of residual moisture had become evident) the components were dried before use—by fusion where possible—and stored over drying agents. Salts were made in most cases by fusion of the carbonates of the alkali metals with the respective acidic oxides.

In the course of the work, several types of apparatus were successively used; that finally adopted is sketched in Fig. 1.

Efficiencies of anode and cathode reactions were estimated by weighing or other direct methods. Anode efficiencies were 100%, or slightly greater where chemical dissolution was appreciable, and this, combined with low cathode efficiencies, often caused a change in bath composition with life for which allowance had to be made.

In the early experiments, a frequent source of trouble was the formation of an overgrowth, both of a general nature and in a more inconvenient form as a "bridge." The latter was a brittle and plate-like growth of metal which extended on the surface of the melt from the cathode towards the anode, ultimately making contact with it. The cause of bridging was traced to the effects of residual moisture in the melt, whereby hydrogen was liberated at the cathode and rather slowly reduced the melt forming tungsten metal, partly at the cathode as a spongy overgrowth, and also—through the formation of a raft of gas bubbles on the melt surface—in the form of a bridge. The oxidised hydrogen returned thus to the melt acted cyclically and continued to cause overgrowth formation. While the defect could be minimised by those measures aiding escape and removal of the gas (high temperature and more fluid melts), complete prevention was accomplished only by the thorough drying techniques referred to above.

Examination of Reported Work.

(a) *Tungstate Melts*—Van Liempts' two baths were tested, but the product was chiefly tungsten bronze with—in some cases—a thin layer of coherent metal beneath.

Gibson's sulphide bath⁷⁶ gave a powdery deposit. In both cases, efficiency was very low.

(b) *Phosphate Melts*.—Hartmann's bath (held in a silica vessel) produced small quantities of a black, brittle deposit consisting chiefly of β -tungsten at low temperatures and α -tungsten above 700°C . Similar results were obtained from the bath of Fink and Ma. Fig. 2 shows a deposit which X-ray analysis showed to be substantially pure β -tungsten.

(c) *Borate Melts*—From the most successful of the baths reported by Fink and Ma²⁵, consisting of 2:1 borax: tungstic oxide, it proved possible, above 850°C ., to deposit rather poorly adherent coatings of metal at low efficiency.

(d) *Chloride Melts*—No satisfactory deposits were obtained from various chloride melts; in most cases a small quantity of dark powdery α -tungsten was collected. It is interesting to note that no β -tungsten was formed, even when the temperatures were as low as 500°C .

Examination of Borate Melts.

As stated above, the only deposits of any promise were obtained from the rather viscous borate melts. These were not really satisfactory, and it was felt that a more fluid bath might prove more effective and, accordingly, mixed borates were tried out.

Constituent	Mol
$\text{Li}_2\text{B}_2\text{O}_4$	4
$\text{Na}_2\text{B}_2\text{O}_4$ or $\text{K}_2\text{B}_2\text{O}_4$	4
WO_3	1

This bath proved capable of giving fair deposits (see Fig. 3) with acceptable efficiency, over a range of conditions of which the following appeared to be close to the optimum: temperature: 900°C .; current density: 0.02 amp./sq. cm. Based on these conditions, the influence of variation in composition was examined.

(a) *Alkaline Oxide Content*.—Maintaining the same ratio of $\text{B}_2\text{O}_3 : \text{WO}_3$, the alkaline oxide content was varied up to a maximum of 8 mol each Li_2O and K_2O without sensibly improving results.

(b) *Tungstic Oxide Content*.—With 4 mol each $\text{K}_2\text{B}_2\text{O}_4$ and $\text{Li}_2\text{B}_2\text{O}_4$, the WO_3 concentration was varied over the range 1–4 mol. Above 2 mol WO_3 , the melt became more viscous and the efficiency fell. A typical deposit is illustrated in Fig. 4.



Fig. 5.—Deposit from borate-chloride melt. $\times 600$

(c) *Boric Oxide Concentration*—A series of melts was made up with a fixed ratio of alkali to tungsten content and varied boric oxide content. In general, the best results were obtained with the more acidic types of melt, where the ratio Li_2O (or K_2O) : B_2O_3 did not exceed 1 : 1. The strongly alkaline melts gave poor results until, when this ratio exceeded 7 : 2, there was no deposition and the tungsten cathode supports were rapidly eroded.

(d) *Borate-Chloride Melts*.—Preliminary trials had shown that, while some deposition could be achieved with many baths, the deposits were more coherent from those containing some "glassy-type" components, such as borates or phosphates. Nevertheless, additions of alkali chlorides had been favoured in such baths by some earlier workers to improve fluidity and conductivity. A series of melts was therefore made up to test the value of such additions, based on the ratios:—

Constituent	Mol
$\text{Na}_2\text{B}_2\text{O}_4$	n ($n = 0$ to 8)
NaCl	$8-n$
WO_3	1

As the concentration of chloride was increased, the deposit became less satisfactory, with marked "treeing," and a tendency for deposition of bronzes. With concentrations of chloride of 4-5 mol, the melts separated into two layers, and from one of these the deposit consisted of loose cubic crystals of metal (see Fig. 5).

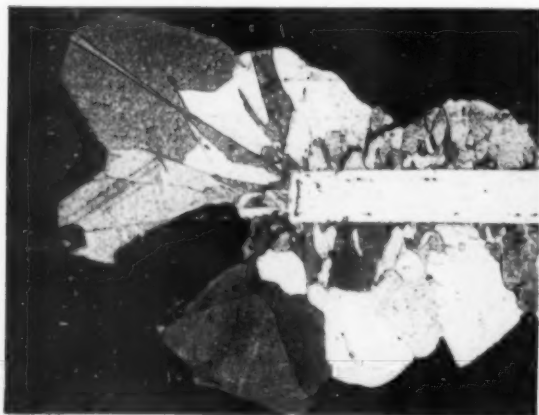


Fig. 6.—Deposit from preferred melt;
C.D. 0.005 amp./sq. cm.

$\times 50$

(e) *Borate-Phosphate Melts*.—A series of baths was made up, based on the composition:—

Constituent	Mol
$\text{Na}_2\text{B}_2\text{O}_4$	n ($n = 0$ to 8)
NaPO_3	$8-n$
WO_3	1

Apart from the case with n zero, the deposits were quite good over the whole range of compositions tested, although the borate-rich melts had the added advantage of higher efficiencies. A serious practical limitation with phosphate-bearing melts lay in the rapid attack of both platinum and silica vessels.

(f) *Borate-Tungstate Melts*.—In this series the following ratios were used:—

Constituent	Mol
NaLiB_2O_4	n ($n = 0$ to 8)
NaLiWO_4	$8-n$
WO_3	1

The use of mixed salts was enforced by the high melting points of the single tungstates. Where n lay between 1 and 8, the deposits were all quite good, but again the highest efficiencies were achieved with the borate-rich melts.

The most satisfactory deposit of all the above tests (at an efficiency of 76%) was obtained with $n = 6$, in the last series, and this "preferred melt" was selected for further examination.



Fig. 7.—Deposit from preferred melt;
C.D. 0.01 amp./sq. cm.

$\times 250$

Examination of Preferred Melt.

(a) *Temperature*—Operating temperatures for the melts were limited in the lower range by fall in conductivity and fluidity as the melting range was approached and in the upper range by volatility of the components, and an increasing re-solution of the deposit. Reasonably good results could be achieved between about 800° C. and 1,050° C., with an optimum in efficiency and life in the range 850-900° C. Subsequent tests were made at 900° C.

(b) *Current Density*—Table I lists some of the results of varying current density, and it is evident that, while acceptable deposits were obtained even at the highest current densities, the efficiencies tended to fall and, in fact, reproducibility above c. 0.1 amp./sq. cm. was rather poor. As a consequence of a lowered cathode

efficiency, the composition of the bath rapidly changed, the rise in tungsten content leading to a rapid decrease in fluidity. Figs. 6-9 show sections of some of the deposits obtained; Fig. 6 is especially interesting since it shows the rapid development of certain grains to the exclusion of neighbours. In several areas (particularly near the edges of the specimen), contiguous grains were in twinned relationship and the twins grew at equal rates, with consequent rectilinear boundaries. It is evident that on certain crystallographic planes, there was easier growth.

(c) *Periodic Reverse Plating.*—A few preliminary experiments were made using a constant current density and varying the periods of reversal; no improvement in

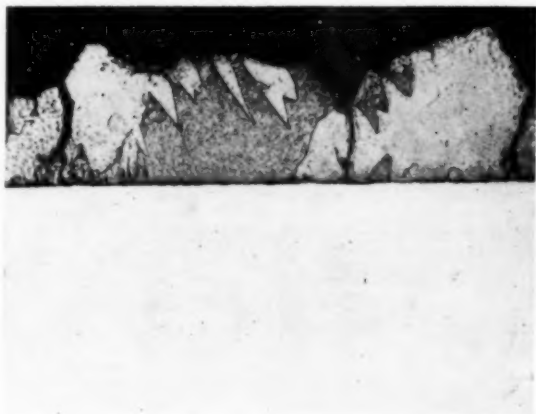


Fig. 8.—Deposit from preferred melt;
C.D. 0.3 amp/sq. cm. $\times 250$

smoothing or efficiency was obtained, and it thus appeared that reducing concentration effects by this means offered no advantage. A second mechanism likely to operate in periodic reverse plating (P.R.P.) is the smoothing of the excrescences, which have been formed on the forward cycle, by field concentration effects on the reverse cycle. Now, owing to the geometry of the system used—a central anode and a ring cathode—the area of the latter was very much the greater. Thus, during the reverse cycle, the (temporary) anode was operating at low current density compared to its cathode current density in the forward cycle. It was felt that it might prove profitable to employ conditions during the reverse cycle which would give electro-polishing, and these conditions were first sought.

A tungsten spiral was made up to simulate the normal cathode while preserving the geometry of the system, should this be important. No conditions in the preferred bath gave electropolishing comparable to that obtainable by aqueous baths, but a distinct polishing effect was achieved at current densities between 5 and 8 amp./sq.

TABLE I.

Experiment	Current Density (amp./sq. cm.)	Time (hr.)	Plating Efficiency (%)	Overgrowth (%)	Appearance
1	0.005	32	100	—	Rather rough
2	0.007	48	80	—	
3	0.01	6	100	—	"Good"
4	0.03	5	87	—	"
5	0.10	2	34	Some	"
6	0.30	0.5	20	"	"
7	1.00	0.1	25	"	"



Fig. 9.—Deposit from preferred melt;
C.D. 1.0 amp/sq. cm. $\times 250$

cm. A voltage-current curve was plotted (see Fig. 10), and it is evident that the "polishing plateau" normally observed covered only a limited range, a result similar to those found by Rowland⁴⁴ when investigating electro-polishing of precious metals in fused baths. Another factor was suspected as being important in P.R.P. experiments: at 900°C., considerable diffusion of tungsten takes place into the base, and the greatest rate of diffusion is clearly at the commencement of plating when the concentration gradient is at its highest. When the first reverse cycle operates, therefore, there is little free tungsten to re-dissolve, and the (temporary) anode is nickel, or rather a nickel-rich alloy. This metal is attacked, forming a pitted surface with oxide scale, and when forward plating recommences it does so on to a completely unsuitable surface. To overcome this in the P.R.P. tests, a preliminary layer of tungsten was laid down by direct plating, and then the P.R.P. was applied using a reverse current density of 5 amp./sq. cm. and various forward current densities (see Table II). The preliminary layer was deposited so that, at 100% efficiency, a thickness of 25 μ would have been obtained, and this thickness was assumed in the estimation of the efficiency of each experiment.

Although efficiencies were never so high as with direct current at low current density, the enormous increase in actual plating rate constituted a real advantage. A

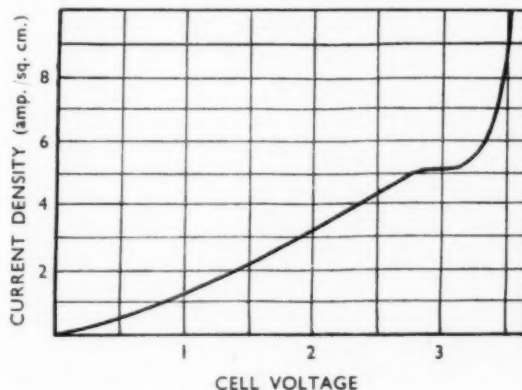


Fig. 10.—Current/voltage curve for preferred melt.

TABLE II.—PERIODIC REVERSE PLATING.

Ex- peri- ment	Each Cycle				Effective Forward Current Density (amp./ sq. cm.)	Total Time (min.)	Effi- ciency (%)	Appearance
	Forward		Reverse					
	Current Density (amp./ sq. cm.)	Time (sec.)	Current Density (amp./ sq. cm.)	Time (sec.)				
1	0-10	56	5	0-4	0-06	180	28	Overgrowth
2	0-22	56	5	0-4	0-18	60	27	Overgrowth
3	0-58	56	5	0-4	0-54	20	40	Overgrowth
4	1-54	56	5	0-4	1-50	7 $\frac{1}{2}$	51	—
5	0-68	50	5	5	0-18	60	27	Overgrowth
6	1-04	50	5	5	0-54	20	25	Overgrowth
7	2-15	50	5	5	1-50	7 $\frac{1}{2}$	35	—
8	5-0	50	5	5	4-50	3	21	Overgrowth
9	0-68	10	5	1	0-18	30	60	Overgrowth
10	1-04	10	5	1	0-54	20	42	Overgrowth
11	2-15	10	5	1	1-50	7 $\frac{1}{2}$	31	Overgrowth
12	5-0	10	5	1	4-50	3	30	—

useful comparison may be made when it is remembered that from Experiments 8 and 12, in about 3 minutes $c. 75\mu$ of tungsten were deposited, which at 0-01 amp./sq. cm. would require $c. 12$ hours. It is possible that the heating effect of the large currents passing itself acted beneficially, for in some cases more than 100 watts were being dissipated in the cell.

The structures of some of the deposits are illustrated in Figs. 11-14, and it may be noted that the P.R.P. deposit appears to be completely continuous with the preliminary layer, while the structures do not appear to be very dependent upon conditions.

A preliminary layer deposited at low current density was also tested for its suitability as a basis for subsequent deposition at high current densities using direct plating, but without success.

(d) *Composition of Preferred Melt.*—Apart from a hope that an improvement in the deposit or the efficiency at high current densities might accrue, there was a further reason for examining the possibilities of modifying the melt composition, for it was not very convenient to use such a reactive mixture at such high temperatures. It was, at one time thought that the high temperatures were necessitated by the intrinsic nature of metallic tungsten, but this view could not be reconciled with the fact that good coatings could be obtained by other methods at temperatures several hundreds of degrees lower than electroplating temperatures, and at quite fast rates. It was more probable that the controlling factors were, rather, the viscosity and resistivity of the bath, both of which increased rapidly at lower temperatures, and it

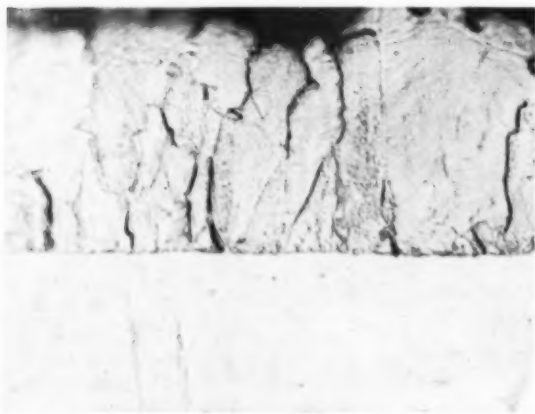
Fig. 11.—Periodic reverse plating. Experiment 9. $\times 500$

TABLE III.—ELECTROCHEMICAL SERIES IN PREFERRED MELT.

Material	Potential at 750° C. (volts)	Potential at 900° C. (volts)
Chromium	-0-97	-0-92
F.I.29	-0-95	—
Mild Steel	-0-95	—
Tungsten	-0-85	-0-6
Molybdenum	-0-85	—
Carbon	-0-8	—
Nickel	-0-7	-0-7
Hydrogen*	-0-6	—
Copper	-0-6	—
Platinum	-0-0	—
Gold	+0-1	—
Oxygen	+0-2	—

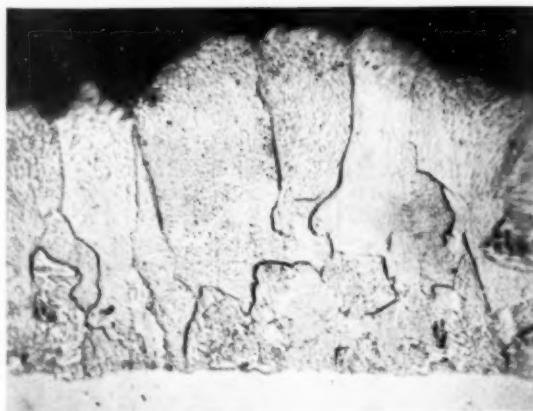
* In a moist melt.

was felt worthwhile to make a limited examination of the possibilities of using lower melting point mixtures. The programme was deliberately limited by basing research upon the preferred melt, and by avoiding the use of salts which were more reactive, formed limited miscibility systems, or had restricted solubility for oxides of tungsten.

It was decided to investigate the influence on fluidity of variation in ratios of the amounts of the components of the preferred melt. Firstly, thermal analysis was used to study the effect of WO_3 content, by establishing, at least approximately, the equilibrium diagram of the pseudo-binary system: $(2 NaLiWO_4 + 6 NaLiB_2O_4) - WO_3$.

For convenience these are referred to as *A* and *B*, respectively.

With concentrations of *B* greater than *A*: $3B$, the solidus and liquidus rose rapidly. Within the range *A*: *B* to *A*: $3B$, the solidus rose from 500 to 600° C., the

Fig. 12.—Periodic reverse plating. Experiment 10. $\times 500$

liquidus remaining near 650° C., and plating trials indicated that there was little to choose between the deposits. The system $NaLiWO_4-NaLiB_2O_4$ was next studied, and it was found that the lowest fusion range lay at high tungstate concentrations. Unfortunately, this reduction in melting point was lost on addition of WO_3 , so that, in fact, the preferred melt itself had the lowest fusion range. Plating trials again showed that excellent deposition could be carried out over a range of compositions, but that the preferred melt—somewhat fortuitously—lay near the optimum.

The finally preferred melt was found to operate very satisfactorily if a few precautions were observed to maintain the composition fairly constant. A life of several hundreds of ampere-hours with a bath of about

100 g. could be expected before the tungsten content had risen too high for good results. To prevent moisture pick-up, the bath was kept molten between runs, or—if it was required to be kept for long periods—it was the practice to pour the melt on to a steel tray to effect rapid cooling and the glassy mass was broken up and stored in sealed vessels.

(e) *Mechanism of Deposition*—The experimental work described above was essentially of an empirical nature, and afforded little information on the mechanism of the deposition. However, several trials were made of plating from a melt held in a platinum vessel heated by H.F. induction. This made possible the use of a cool Pyrex enveloping vessel, which facilitated more perfect atmosphere control while permitting direct observation. Under

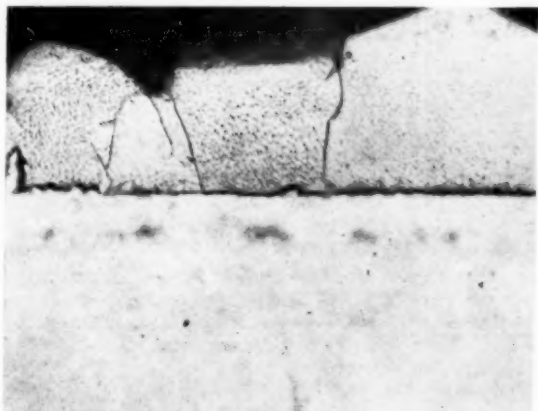


Fig. 13.—Periodic reverse plating. Experiment 11. $\times 500$

these conditions, an examination was made of the behaviour of several melts, in an endeavour to arrive at some understanding of the nature of the electrode reactions. In this study, the large area vessel was used as an auxiliary electrode—since some indication could be obtained of the ease of ion discharge at a given electrode and the reference electrode under conditions where no effective current passes between them²²—the p.d. being measured on a high impedance valve voltmeter.

The first tests made were to establish an "electrochemical series" in the preferred melt (see Table III), using platinum as an arbitrary zero. It was found that



Fig. 14.—Periodic reverse plating. Experiment 12. $\times 500$

gold was more noble than platinum, and so it was chosen as electrode material in the subsequent tests. From the table it can be seen that steels are less noble than tungsten, and from this arises the difficulty in plating them which had been observed in the preliminary search for cathode materials.

Voltage/current curves were now plotted for the following three melts, both dry and moist: (1) NaLiB_2O_4 , (2) $6\text{NaLiB}_2\text{O}_4 + 2\text{NaLiWO}_4$ (called melt P-1) and (3) $6\text{NaLiB}_2\text{O}_4 + 2\text{NaLiWO}_4 + \text{WO}_3$ (P). When gold electrodes were used, the curves were of the normal type, with a change in slope at the "decomposition potential"; the results are summarised in Table IV.

Some tentative observations may be made on these results:—

- (1) The simple borate melt has a decomposition voltage of 1.5V. If it is assumed (see Andrieux⁴⁵ and Zarzycki⁴⁶) that the only cations present are the alkali metal ions, this voltage refers to the conditions for their discharge, oxygen being discharged at the anode. In fact, no gas or liquid metal was observed at the cathode, so it must be assumed that the discharged metals reduced the boric oxide there to form boron. The gold cathode was indeed found to have been embrittled.

In the presence of moisture, hydrogen was evolved at an applied potential difference of 1.3V., i.e., 0.2V. below that for the alkali metals. When a tungsten cathode was used, the decomposition

TABLE IV.—DECOMPOSITION VOLTAGES OF MELTS.

No.	Melt	Cell Potential for Gas		Decomposition Voltages			Back E.M.F. (volt)	Materials			Electrode Potential $i = 0$		Remarks
		at Anode (volt)	at Cathode (volt)	Anode-Cathode (volt)	Cathode* (volt)	Anode* (volt)		Vessel	Anode	Cathode	Anode* (volt)	Cathode* (volt)	
1	LiNaB_2O_4	1.3	1.3	1.2-1.3	1.1	0.2	—	Pt	Au	Au	0.1	0.1	Moist c. 750° C.
2	LiNaB_2O_4	1.6	—	1.5-1.6	1.3	0.3	1.5	Pt	Au	Au	—	—	Dry c. 750° C.
3	LiNaB_2O_4	1.7	—	1.6-1.7	1.5	0.2	—	Pt	Pt	Pt	—	—	Dry c. 750° C.
4	LiNaB_2O_4	—	—	1.2	—	—	—	C	Pt	W	—	—	Dry c. 750° C.
5	LiNaB_2O_4	0.45	—	0.4	—	—	0.4	C	C	W	—	—	Dry c. 750° C.
6	P-1	1.0	1.0	—	0.9	0.1	1.0	Pt	Au	Au	0.02	0.02	Moist c. 750° C.
7	P-1	1.1	—	1.2-1.3	1.0	0.3	1.1	Pt	Au	Au	—	—	Dry c. 750° C.
8	P-1	1.1	—	1.2	—	—	1.2	Al_2O_3	Pt	Pt	—	—	Dry c. 750° C.
9	P	1.1	—	1.1	0.9	0.2	1.1	Pt	Au	Au	0.1	0.1	Dry c. 750° C.
10	P	—	—	0.1	0.9	0.8	0.1	Pt	W	Ni	0.1	0.1	Dry c. 750° C.
11	P	—	—	0.1	0.9	—	0.1	Pt	W	W	0.1	0.1	Dry c. 750° C.
12	P	—	—	0.1	—	—	0.1	Pt	W	W	0.1	0.1	Dry c. 750° C.
13	P	1.1	—	1.1	0.8	0.2	1.1	Pt	Au	Au	0.1	0.1	Dry Check
14	P	—	—	1.3	—	—	—	C	Pt	Pt	—	—	Dry 700° C.
15	P	—	—	1.1	—	—	—	C	Pt	Pt	—	—	Dry 800° C.
16	$\text{WO}_3 + \text{B}_2\text{O}_3$	—	—	—	—	—	—	—	—	—	—	—	Too viscous to test

* p.d. between electrode and auxiliary electrode (the platinum crucible).

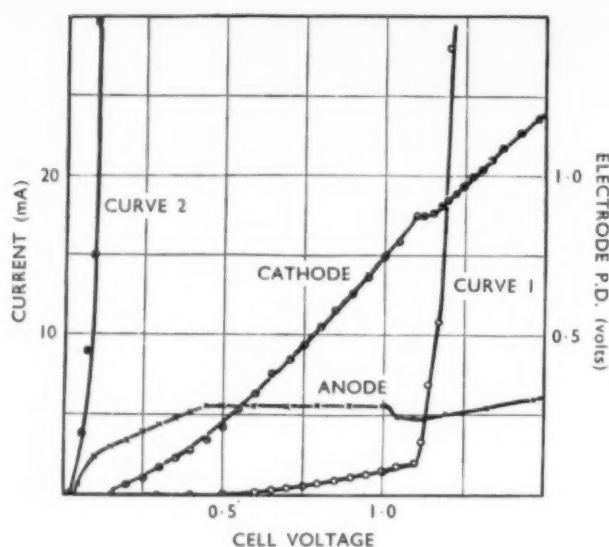


Fig. 15.—Current/voltage curve for preferred melt.

voltage was lowered to 1.2V.: presumably the tungsten acted in some favourable way upon the discharge of the ions reducing the overvoltage. There was a further, and large, reduction in decomposition voltage with carbon anodes, presumably because of a different anode reaction or a lowered oxygen overvoltage.

- (2) The P-1 melt had a decomposition voltage of 1.2V.—lower than that of the borate melt—and this appeared to be mainly associated with a lower cathode potential. Again, hydrogen was evolved from moist melts at a lower cell voltage.

In these experiments with inert anodes, no tungsten plating was observed, although it may be remembered that, using a tungsten anode, some plating had been obtained previously with this melt, albeit at low efficiencies. The poor efficiencies meant, of course, that the melt grew richer in tungsten oxide content, and, in fact, the efficiencies rose steadily with usage of this melt.

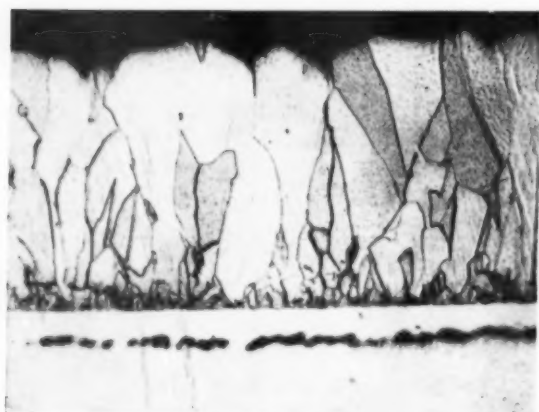


Fig. 16.—Thick deposit from preferred melt. $\times 250$

TABLE V.—HOT-HARDNESS OF DEPOSITS COMPARED WITH BULK TUNGSTEN.

Temperature ($^{\circ}$ C.)	Hardness (V.P.N.)	
	Bulk Tungsten	Deposit
20	405	425
100	250	385
200	180	290
300	150	167
400	120	147
500	110	116
600	82	91
700	67	83
800	65	71

- (3) The preferred melt behaved similarly to the previous two melts when inert electrodes were used, and this seems to suggest that the same mechanism was operating in all three—presumed to be a primary discharge of alkali metals. If, alternatively, tungsten ions were discharged directly, then the deposition potential for tungsten must be not greatly below that for the alkalies, but still above that for hydrogen. It may be remarked here that during the experiments with gold electrodes in the preferred melt, no tungsten was observed to be deposited until the applied e.m.f. was greater than 1.1V and the cathode-platinum potential c. 0.87V.

In Fig. 15 a plot of the cell-voltage/current curve is shown for gold electrodes (Curve 1) and tungsten electrodes (Curve 2). On the same diagram is plotted the p.d. between either electrode and the platinum crucible against the cell voltage, using gold electrodes. It may be noted that the p.d. between the anode and the crucible rose to a maximum of 0.28V., remained constant until oxygen began to flow, when it first dropped to 0.23V. and then rose steadily with cell voltage. This may be taken as indicating an electrode potential for oxygen with respect to platinum of ± 0.23 V., and an oxygen overvoltage at gold of 0.05V. At the cathode, the potential rose steadily until the decomposition voltage was reached, when there was a slight plateau in the cathode-platinum potential curve at a value of c. 0.88V., corresponding to the discharge of ions. Above the decomposition point, the slope of the current/cell-voltage curve rose rapidly, and from this portion of the curve the resistance due to the melt itself was estimated, and found to be less than 0.1 ohm. This low resistance means that when 1.1V. was applied across the cell, the potential drop due to the melt was less than 0.2 mV., i.e., it could be

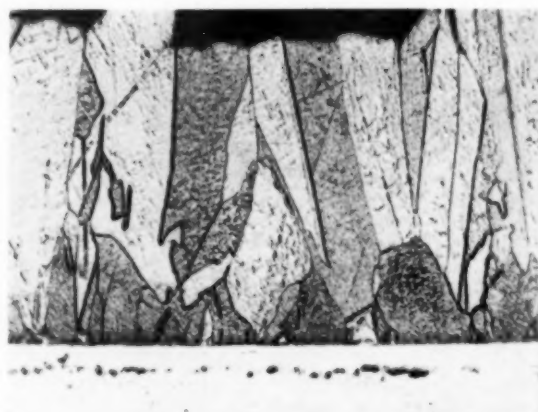


Fig. 17.—Thick deposit from preferred melt. $\times 150$

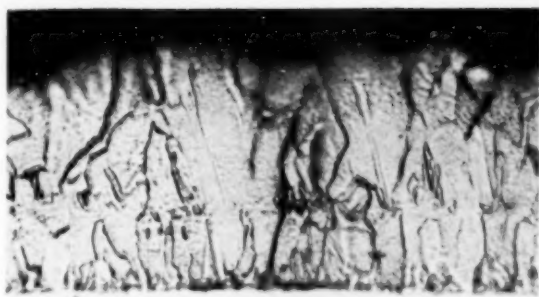


Fig. 18.—Two-stage deposit from preferred melt. $\times 600$

disregarded in comparison with the p.d. between the electrodes.

When tungsten electrodes were used, the decomposition voltage was negligible, from which it is reasonable to deduce that the anode reaction is the reverse of the cathode reaction, with no overvoltage or other polarisation phenomena at either electrode.

Nature of the Deposits.

Several samples of the deposits after removal from the basis metal were analysed spectrochemically, and the results compared well with tungsten wire; two analyses are given below—*A* was deposited at 0.01 amps./sq. cm. and *B* at 1 amp./sq. cm.; *C* is representative of pure tungsten wire.

	%Cu	%Ti	%Mo	%Al	%Cr	%Fe	%Pb	%Mg	%Si	%B
A	0.001	0.004	0.03	<0.001	0.001	0.006	0.001	0.002	0.004	Not detected
B	0.002	0.0004	0.01	0.002	0.002	0.07	0.001	0.002	c.0.1	Not detected
C	0.001	0.0005	0.02	0.001	0.001	0.003	<0.001	0.001	0.004	—

The deposits were examined both visually and by making microsections, the latter in some cases obliquely, to emphasise surface form or to show up thin layers. To minimise steps in the section due to variation in hardness of the phases present, polishing was effected with two grades of diamond dust. In many cases, the surface was protected by a coating of hard nickel. Etching reagents were as follows:

- (a) For tungsten: Murakami's reagent: 10% KOH—1 part
35% $K_3Fe(CN)_6$ — 1 part
- (b) For nickel: (i) Precision No. 247
(ii) 5% $(NH_4)_2S_2O_8$
5% KCN

All good deposits were free from pores or pockets of other material, and the microstructure of columnar grains was surprisingly constant, showing negligible variation with changing plating conditions or melt composition. A common feature was the coarsening of grain size as the thickness of the deposits grew, which was presumably the result of more rapid growth of favourably oriented grains. (See Fig. 16). With thick deposits, rectilinear boundaries were frequently observed (see Fig. 17), and these two facts would suggest that the deposits were likely to develop a preferred orientation. This was found

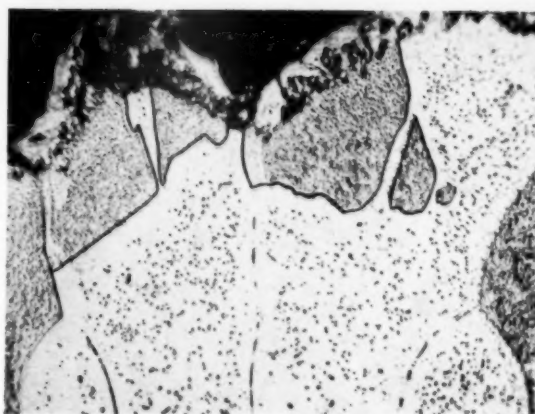


Fig. 19.—Deposit heated to 1,600° C. for 10 mins. $\times 250$

to be the case, a rather weak tendency being observed for [100] direction to lie normal to the surface.

The coarsening with growth argues a greater ease of growth than nucleation of new grains, and this was confirmed by interrupting plating, grinding and polishing the surface, and then proceeding with the plating. The structure of the original grains was continued, as is illustrated in Fig. 18. There was no other evidence that the structure of the basis metal had any influence on the deposit. It should be remembered that nickel and platinum have dissimilar structures to tungsten, but each has extensive solubility for the metal, and it was rather surprising to note that the tungsten deposit always had much finer grain size initially than the basis metals.

It was noted that all the deposits were brittle, readily fracturing in an intercrystalline manner, although this should not be ascribed to the plating process *per se*, since tungsten made by melting or by conventional powder metallurgy is invariably brittle if it has a structure similar to that seen in the authors' deposits.

Mechanical tests were confined to hardness and hot-hardness tests. Room temperature hardness of the deposits was always near 450 V.P.N., a value similar to those observed for conventionally produced tungsten in the fully annealed state. The hot hardness ran parallel with such material (see Table V.).

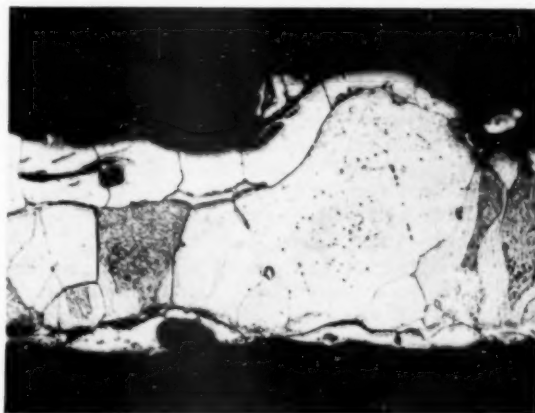


Fig. 20.—Deposit heated to 1,800° C. for 10 mins. $\times 250$

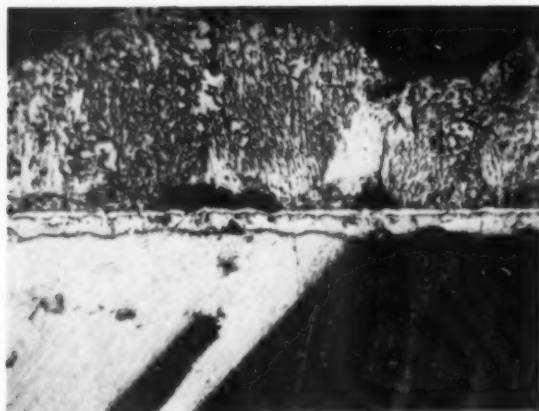


Fig. 21.—Deposit on nickel (etched for tungsten and nickel). $\times 500$

A typical sample was subjected to heat treatment. At 1,400° C. there was no sign of grain growth or recrystallisation; above 1,600° C., the columnar structure gave way to a somewhat more equiaxed structure, but even at 1,800° C., no severe coarsening had set in (see Figs. 19 and 20). Room temperature hardness remained unaffected.

It proved very difficult to make accurate measurements of adherence, chiefly due to the brittle nature of the deposits, but bend tests and other, rather subjective, observations suggested that the adherence of the deposits to nickel was higher than their coherence. From hardness measurements and a comparison with conventional metal, the coherence as measured by ultimate tensile strength may be estimated as near 100 kg./sq. mm.

Good adherence would be expected, of course, from the evidence of extensive interdiffusion between the deposit and the nickel basis metal. In this diffusion, in fact, lies a source of weakness since, at 900° C., a layer of the β -phase must form, and such intermetallic compounds are notably hard and brittle with little resistance to shock. The previous micrographs have been on samples etched only for tungsten, but the diffusion zones are clearly shown in Fig. 21 and can, of course, be simply related to the horizontal section at 900° C. through the phase diagram.

With regard to basis metals, the required properties are adequate rigidity at 900° C. and inertness towards the bath at this temperature. For aqueous plating, inertness is less imperative, since the surface may be immediately "sealed" by the deposit, but, in fused baths, diffusion can at first be rapid compared with deposition rate. As cheap basis materials, many metals and alloys have been tested—especially carbon- and alloyed steels—but only nickel has been found useful. Completely satisfactory deposits have been made on to nickel-plated steels, with a layer of nickel some 5–10 μ thick (see Fig. 22).

For the fabrication of tungsten tubes and cylinders, the metal has been electrodeposited on mandrels of nickel and the latter subsequently dissolved away.

Theoretical Discussion

All the processes of aqueous plating have one common feature—they are unified by the presence of an ionising medium common to them all. This enables the various

data such as deposition potentials and the like to be referred directly or ultimately to a universal standard, and has thus permitted the accumulation of a mass of integrated information which is immediately applicable to the solution of many practical and theoretical problems. In non-aqueous systems, the position is quite different. Where solvents other than water are used, such as organic liquids, ammonia, etc., there are often points of contact with the conventional electrochemistry of aqueous solutions, and it not infrequently happens that the same concepts are applicable directly, with a more-or-less easily converted set of numerical values.

In fused salt systems, each must be examined as a separate entity, and the experimental results obtained from its investigation are rarely of direct value in other, even similar, systems. A further distinction between fused melts and aqueous electrolytes lies in the great disparity between the concentrations of the ionised components in the two cases, since in fused salts this concentration may be 100%. Finally, in the field of aqueous plating, the transport number of cations and anions are at least comparable, since even the most mobile ions rarely transport more than 90% of the current. With fused baths, however, virtually the whole of the current may be transported by certain ions⁴⁸.

Apart from theoretical considerations, the experimental approach to an improved understanding is more difficult for fused baths than for aqueous plating. A standard reference electrode is not immediately available for the study of the separate electrode reactions. Hartmann used such an electrode in his examination of the phosphate melts, employing a porous ceramic vessel for his cell. No ceramic material inert to the authors' melts and, hence, suitable for the purpose, was discovered. If it were possible to construct a satisfactory cell, it would be furthermore necessary to establish that the liquid junction potential could be neglected.

An explanation of plating of tungsten from melts where the metal is held as simple cation would seem to offer no problems. Although this is no doubt an oversimplification, especially in those baths⁴⁹ where anions other than halides are included, it may be supposed that, when these conditions obtain, the tungsten is deposited directly by discharge of its ions at the cathode if the deposition potential be lower than that of other cationic species present in the melt. It is, of course, likely that the mobility of the tungsten ion is lower than that of alkali metals present, but unless conditions are such as to cause excessive concentration polarisation, pure tungsten is likely to be deposited directly. In melts, the lighter alkali-metal ions can be expected to be more mobile than tungsten-bearing ions (their comparatively low mobilities in aqueous baths are due to hydration of the ions and a consequent increase in their effective size and mass).

When the tungsten is present in anions, its deposition at the cathode may be explained in two ways:

- (a) Dissociation of the anions to form some metallic cations.
- (b) The discharge of cations of some other element present—the primary cathodic reaction—and the chemical reaction of this element with melt constituents to deposit metallic tungsten.

Each process has had its own protagonists, and it is probable that under certain conditions one can be stated to be dominant.

Van Liempt's work was confined to melts of simple alkali metal tungstates. On electrolysis, he considered that sodium was discharged at the cathode and then reacted to form tungsten in neutral melts, or bronzes in acid melts, so that an excess of alkali would thus favour tungsten metal deposition. Unfortunately, such excess would also give the melt greater solvent power for the metal, so that electrolysis was actually most effective in neutral or slightly acid baths. The bronzes produced at the cathode are unstable towards heat if they are not in contact with an acid melt, explaining the growth of tungsten on the cathode beneath a layer of bronze crystals.

The papers by Hartmann *et al* were devoted to the electrolysis of phosphate melts. Their findings, briefly, were that tungsten and phosphorus were co-deposited in baths based on phosphoric acid or simple phosphates, but that pure metal could be obtained from alkaline melts. Hydrogen was more readily deposited than tungsten, so that the last traces of moisture had to be removed before satisfactory deposition could be achieved.

They explained these results by supposing that in alkaline melts (i.e., those with pyrophosphate) the tungsten was present as tungstate ions, while in acid melts stable phospho-tungstate complexes were formed, and, from these, the tungsten had a high deposition potential, due to the depressed concentration of tungstate ions. The complexes could be reduced at the cathode, but such a potential was required that phosphorus was also deposited. At low temperatures, and high tungstic oxide concentrations, bronzes formed preferentially. As these are formed from VI- and IV-valent tungsten, and are stable at low temperatures, all the conditions favourable for their formation obtain at the cathode and promote their production.

Fink and Ma had greatest success with melts of borates and phosphates, and it was for these that they advanced their hypothesis proposing that metallic sodium was deposited at the cathode as a continuous film of vapour, and there caused polarisation to an extent dependent upon the thickness and "tenacity" of the film. An extension to this hypothesis supposed that the thickness of the film had to be of a certain value for optimum results, when re-solution of tungsten and interference with the deposition were minimised.

The later paper by Andrieux⁴⁵ gives a general dissertation upon his own work and that of his co-workers, and from a consideration of the results he comes definitely to the conclusion that in borate melts the boric oxide acts in the role of "support," and as an ionising dielectric, and that most other oxides are ionised into oxygen and metal ions. Zarzycki's cryoscopic experiments on borates⁴⁶ lend support to Andrieux's theories, although his conclusions and assumptions have been criticised by Bockris (*loc. cit.*).

The cations discharged are those of sodium, and this metal will react with the B_2O_3 present. As sodium is a poor reducing agent for boric oxide, the product is always contaminated with sodium and lower oxides of boron.

Andrieux states that if to boric oxide are added metallic oxides of free energies of formation lower than that of boric oxide, the corresponding metal will be liberated at the cathode as a primary product. Among other examples, he cites the addition of WO_3 and the deposition at the cathode of metallic tungsten.

The essential problem is whether tungsten is produced by the primary cathode reaction of discharge of ions, or

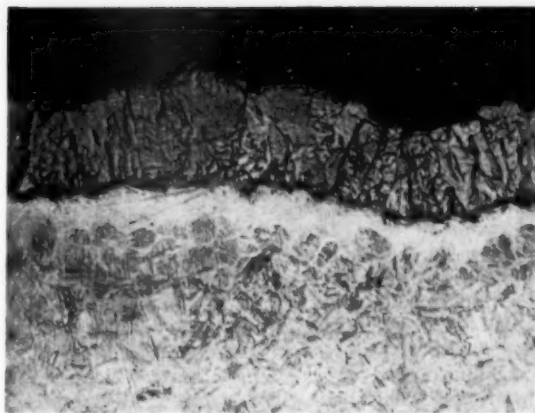


Fig. 22.—Deposit on nickel-plated steel. $\times 600$

by reduction of a melt constituent by liberated alkali metals. It cannot be claimed that any conclusive evidence is available from the present work to exclude completely either possibility. Four facts seem to indicate, however, that in our finally preferred bath, deposition of tungsten takes place directly.

- (1) The apparent reversibility of the process when tungsten electrodes are employed, coupled with electrical efficiencies near 100%.
- (2) The general metallurgical appearance of the deposits, which are dense, coarse grained and free from stress.
- (3) The high purity of the deposits over a range of current densities.
- (4) No deposition of alkali metals has been observed under any conditions.

It is perhaps worth considering the second point in greater detail. If the primary product were, say, sodium, and this reacted with the melt, a continuous layer of tungsten could be built up on the cathode only if the reduction occurred preferentially at this surface. Otherwise it must be expected that a film of sodium would be developed, in which case tungsten must be deposited at the outer surface of this film in the body of the melt, when the deposit would be of a powdery non-adherent form.

It is confirmatory evidence that when tungsten is known to be formed by a secondary reaction (as when hydrogen is present), the liberated metal appears as aggregates of fine particles with poor adhesion to the main body of the cathode. In this case, as must be expected, the effective efficiency of electrolysis is always very low.

If tungsten is deposited by discharge of tungsten cations derived from a tungstate complex, then concentration effects will be particularly severe, since the degree of ionisation of the complexes is small and the absolute concentration of tungsten cations is low. The preferred melt contains a small concentration (c. 10 mol.%) of tungstic oxide. An increase in this concentration might be assumed to increase the tungsten cation concentration, and thus give improved plating (or at least the possibility of using higher current densities). Indeed, as the experiments on the tungstic oxide concentration showed, with further additions of oxide, plating continued to be satisfactory, and old baths which were operating well

were characterised by their increased tungsten content. A practical limit to these additions is set, however, by the simultaneous increase in viscosity and resistance of the melt, with the consequent depression in plating quality. The composition of the preferred melt seems to be the best compromise between these opposing tendencies.

The nature of the voltage/current curve for the preferred melt, using tungsten electrodes, suggested immediately that tungsten is plated reversibly, and there seems no reason to propose a more indirect process. Since the mobilities of the alkali metal ions, and presumably also their concentration, greatly exceed those of any other ions which may be presumed to be present, virtually the whole of the current must be carried by them, whatever ions are discharged.

The authors' advance as a hypothesis, which does not appear to conflict with the experimental facts, that ionisation of the melt components proceeds as follows:

- (1) $\text{Na}_2\text{B}_2\text{O}_4 \rightleftharpoons 2\text{Na}^+ + \text{O}^{2-} + \text{B}_2\text{O}_3$ (after Andrieux)
- or (1a) $\text{Na}_2\text{B}_2\text{O}_4 \rightleftharpoons 2\text{Na}^+ + \text{B}_2\text{O}_4^{2-}$
- (2) $\text{Na}_2\text{WO}_4 \rightleftharpoons 2\text{Na}^+ + \text{WO}_4^{2-}$
- (3) $4\text{WO}_3 \rightleftharpoons 3\text{WO}_4^{2-} + \text{W}^{6+}$
- (4) $4\text{O}^{2-} + \text{W}^{6+} \rightleftharpoons \text{WO}_4^{2-}$

The boric oxide can be assumed to act as an ionising medium which is inert relative to the other components. Apart from this inactive role, the boric oxide (and borates) can depress the concentration of WO_4^{2-} ions by complexing as boro-tungstates, and thus drive reactions (3) and (4) to the right. If the existence of tungsten cations is assumed, the reaction at a tungsten anode can be simply one of solution with electron loss to form tungsten cations, the reverse taking place at the cathode. These reactions would appear to explain the behaviour of the preferred melt; the fact that plating is very unsatisfactory from P-1 melts (i.e., containing no free WO_3) suggests that reaction (3) is the dominant one for the production of tungsten ions. This would mean that reaction (4) is of little importance.

It may be presumed from this reasoning that any salt capable of complexing the tungstate anions would aid the formation of tungsten cations from a mixture of tungstates with tungstic oxide, and this perhaps explains the success of certain phosphate baths. In the absence of such complexing salts, there is probably a greater tendency to form acid tungstates and, from these, as van Liempt has shown, tungsten bronzes at the cathode.

CONCLUSIONS

No success has been achieved with aqueous baths, in obtaining deposits of tungsten or tungsten-rich alloys with the requisite properties. In fact, the available evidence strongly suggests that the fundamental properties of tungsten in aqueous solution are such as to preclude the possibility of its electrodeposition. It might, however, still be possible to deposit refractory alloys with metals other than the ferrous metals.

In organic solvents, the co-ordination energies of tungsten-bearing ions may be considerably less than the co-ordination energies of the aquo-complexes. There is perhaps a stronger possibility, therefore, of plating tungsten from such solutions, despite the lack of success in the limited approach adopted in the present work. It is felt that a profitable line to study is the electrolysis of solutions of some of the tungsten chelate complexes.

The most valuable part of the present work has been

the deposition of thick, coherent layers of pure tungsten from fused salt baths containing borates and tungstic oxide. To obtain a melt of low viscosity and high electrical conductivity at moderate temperatures, mixed alkali metal salts have been used; the addition of tungstate has also been shown to act advantageously in improving the nature of the deposit, possibly by providing a reservoir of the metal and by improving conductivity. With direct current plating, only with rather low current densities were deposits of good appearance produced at high electrical efficiency, but much faster rates of deposition of equally good appearance can be attained when periodic reverse plating is used under the appropriate conditions.

The operation of the preferred bath presents little difficulty on the laboratory scale if the precautions that have been discussed are taken. Throwing power is good and no limitation to the thickness of tungsten has been encountered up to a thickness of 500 μ . Tungsten samples of different shapes have been fabricated by deposition and subsequent dissolution of the basis metal: the aims set out in the introduction have, thus, largely been fulfilled.

The main practical objections to the method are set by the reactivity of the melt. Although corrosion of cheap basis metals such as steel can be simply overcome by nickel plating, attack of the containing vessel will probably be the greatest difficulty if the method is to be used on a larger scale. There do not seem, however, to be any obvious reasons why the method could not be adopted as a production technique on a small scale. Whether this is worthwhile depends upon a consideration of the relative advantages and disadvantages of electrodeposition against the other methods of plating tungsten.

The theoretical aspects of electrodeposition from the fused salt baths have been treated rather extensively, in the belief that such baths must in the future become of greater importance for the electrowinning or electroplating of many of the refractory metals. It is hoped that the information provided may assist in the better understanding of such results.

Acknowledgments

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Aluminium Houses for Colombia

A \$3,000,000 contract has recently been awarded to British suppliers by the housing organisation of the Government of the South American Republic of Colombia. It covers the purchase of 3,200 Kingstrand aluminium houses. The housing organisation—the Instituto de Credito Territorial—is acting in pursuance of the Government's desire to deal with a shortage of rural housing; Colombia estimates that 500,000 rural housing units are needed at present, and that the shortage is increasing at the rate of 8,000 a year.

The Kingstrand house is of particular value to them. Because of terrain and transportation problems, construction using local materials is difficult in Colombia. Each of the frameless, light aluminium houses is delivered in a single compact box only 12 ft. long, 3 ft. wide and 1 ft. thick. They can easily be transported to remote regions by jeep, truck or aeroplane, and erected by unskilled labour within a few hours of arrival at the site. The Kingstrand house is adaptable to a wide range of climatic conditions, but is particularly suitable for tropical areas, where its resistance to vermin, fungus and corrosion is specially important, and where, too, its remarkable coolness under direct sun is highly valued. A wide range of sizes and designs is possible. The Colombia shipments are made up of four different units, ranging from a three-room house and verandah (375 sq. ft.) to a unit of six rooms and two verandahs (812 sq. ft.).

The history of the Kingstrand house is one of co-operation in the widespread activities of the Aluminium, Ltd., Group. The idea, originating in Canada with Aluminium Laboratories, Ltd., was developed by Northern Aluminium Co., Ltd., in Britain. Sales are handled by the group international selling companies, including Aluminium Union, Ltd., in London. Supplies

of metal from the group Canadian smelters are fabricated by Northern Aluminium Company at their Banbury and Rogerstone works. The actual manufacture and packing of the house are carried out by an independent concern, A. P. Metalcraft, Ltd., Coventry and Shipston-on-Stour.

The United Nations has estimated that more than 15,000,000 families in underdeveloped areas throughout the world lack adequate housing. The Kingstrand house is regarded by housing experts as one possible solution to this problem, and one which offers wide export prospects.

Inco Drives Surface Mining Tunnels

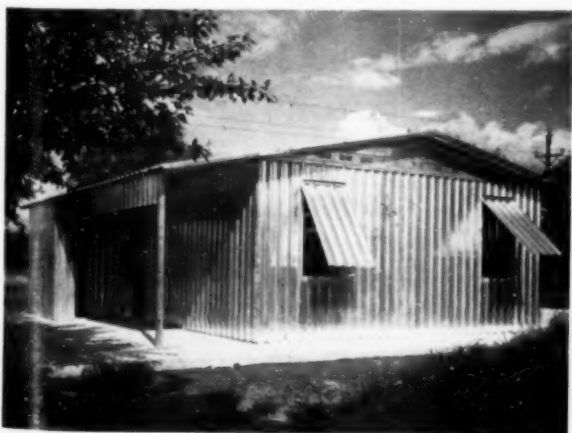
In an engineering project unusual in open pit mining, the International Nickel Co. of Canada, Ltd., is driving two vehicular tunnels with a total length of 2,200 ft. in the walls of its Frood-Stobie Open Pit, in the Sudbury District of Ontario, to permit greater recovery of ore by low-cost surface methods.

The tunnels will take the place of sections of the main ramp road which winds for almost two miles around the sides of the Open Pit, now nearly 600 ft. deep. When the tunnels are completed, pit traffic will be routed through them, and the affected portions of the ramp road will disappear as the ore over which they lie is mined. The usual surface mining procedure of churn-drilling, blasting and trucking will be used to recover the ore beneath the ramp.

The ore is comprised of a large block in the footwall, as the wall on the underside of a vein or ore structure is known, and a smaller block on the hanging wall, or upper side. A total of 5,000,000 tons of ore is involved.

Originally it was planned to recover the ore by underground methods after all surface mining had been completed and the road was no longer required. The ore would then have been mined by the same methods as are being used in the south end of the Frood section of the pit, and also in the Stobie section, where surface operations have been replaced by blasthole mining carried on from the 600-ft. level underground.

The tunnels will be 14 ft. wide and 15½ ft. high. They will be driven some distance inside the footwall and hanging wall, but parallel to the ramp. The longer tunnel, in the footwall rock, will be 1,800 ft. long. The other tunnel, 400 ft. in length, will be driven in the hanging wall rock. Construction of the longer tunnel has begun and is proceeding at the rate of 100 ft. per week. When both are opened to traffic, trucks will move up through the 1,800-ft. leg, then come out at the south end of the open pit before entering the hanging wall tunnel. A smooth, safe flow of trucks hauling ore from the pit will be controlled by stop-and-go lights at the tunnel portals.



Aluminium Cable Installation

Use of Light Metal for Sheath and Core

WITH the increasing attention now being directed to the use of aluminium conductors for insulated cables in addition to the use of aluminium for sheathing, the cable installation in the new extrusion plant building at British Aluminium's Latchford Lock Works is of particular interest. Although there is nothing novel in the use of aluminium for both conductors and sheaths, this constitutes the first large-scale installation in this country in which aluminium has so extensively replaced the conventional copper and lead.

A natural reluctance to depart from well-established practices and materials may in the past have influenced users and, in the absence of overwhelming technical advantages, of which perhaps weight saving by itself was not sufficient, a strong economic incentive has been necessary to provide an impetus toward change. Price trends, however, particularly in the last year, have moved steadily in favour of aluminium so that, for many types and sizes of cable, a significant and often substantial reduction in cost can be achieved by its use.

Except for the largest power cables, aluminium has been used throughout the installation at Latchford as conductor material, both of rubber insulated wiring cables and also of paper insulated cables of all types, both medium and high tension. Where sheathed cables are used the sheaths also are of aluminium, the only exception here being some large 1.0 sq. in. cables feeding the main medium voltage sub-station switchboard from the transformers.

Details of the installation are given below, with a review of the economics of the scheme relative to the

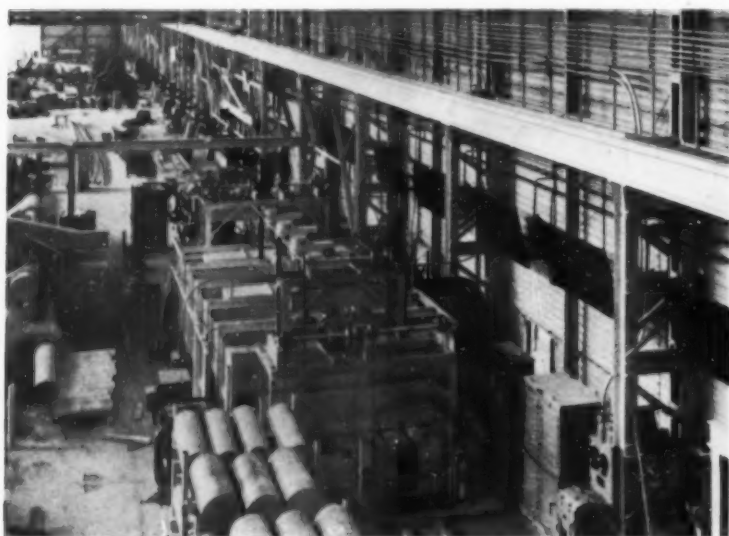
conventional copper or copper/lead alternative. The results show that an all-aluminium cable scheme, including both underground feeder systems and factory or building wiring, offers a significant saving in cost as against a cable installation embodying traditional materials.

Experience on the Latchford scheme also served to confirm that a completely satisfactory installation can be obtained without introducing any significant changes in normal installation procedure. Generally speaking, aluminium-conductor/aluminium-sheath cables were found no more difficult to handle than copper/lead cables, although it must be recognised that, with underground feeders directly buried in the soil, care is necessary to ensure that the special servings are not damaged.

The outstanding technical advantage of weight reduction proved of considerable benefit in the initial running out and slinging of power cables in buildings, although somewhat offset by the extra time required in straightening and in shaping the bends in aluminium sheathed conductors. Whilst it is always advantageous to plan cable routes with the object of avoiding sharp bends, and to keep the bend radii as large as possible, this is not mandatory to the use of aluminium sheaths, since with reasonable care and suitable equipment such cables can be satisfactorily installed even on more complicated routes.

Quantity and Types of Cable

The installation contains approximately 3,000 yd. of all-aluminium paper insulated cable to B.S. 480, and



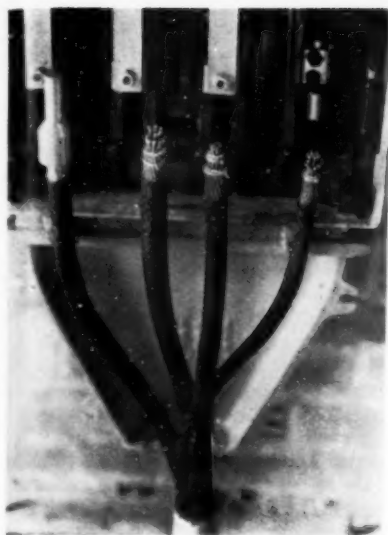
Courtesy of British Insulated Callender's Cables, Ltd.

General view along east side of factory, showing the main cable runs. The smaller amount of supporting necessary for aluminium sheathed cables is well illustrated in the furnace cable terminations.



Courtesy of British Insulated Callender's Cables, Ltd.

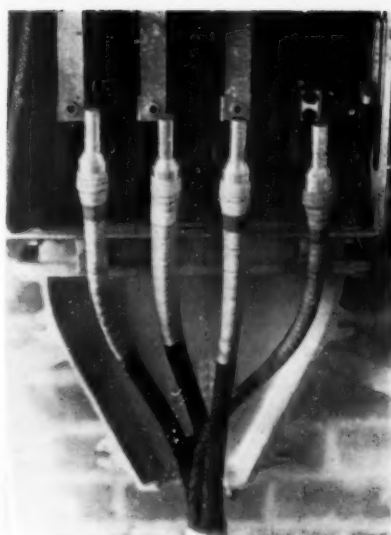
Outgoing 1,100 V. aluminium conductor P.I.A.S. cables from factory sub-station medium voltage switchboard.



Cable terminations for 300 amp. switch fuse unit, showing conductors stepped for soldering.

Completed termination to 300 amp. switch fuse unit.

Courtesy of British Insulated Callender's Cables, Ltd.



Courtesy of British Insulated Callender's Cables, Ltd.

14,300 yd. of aluminium conductor V.I.R. or P.V.C. insulated cable to B.S. 7 or B.S. 2004, of which 4,500 yd. is aluminium sheathed, the remainder being taped and braided. Details of the range of cable types and sizes are included in Table I.

TABLE I.—SCHEDULE OF CABLE TYPES AND SIZES EMPLOYED IN THE LATCHFORD INSTALLATION, TOGETHER WITH APPROXIMATE LENGTHS OF EACH.

Type of Cable	Length installed (yd.)
11 E.F. Paper Insulated, Aluminium Sheathed and Served, Aluminium conductor, aluminium sheath, 3-core 0.15 to 0.30 sq. in.	1,550
11 E.F. Paper Insulated, Bare Aluminium Sheathed, Aluminium conductor, aluminium sheath, 3-core 0.0225 to 0.1 sq. in.	200
1,100 V. Paper Insulated, Aluminium Sheathed and Served, Aluminium conductor, aluminium sheath, 4-core 0.0225 to 0.3 sq. in.	650
1,100 V. Paper Insulated, Bare Aluminium Sheathed, Aluminium conductor, aluminium sheath, 3- or 4-core, 0.0225 to 0.30 sq. in.	850
250 and 600 V. Rubber or P.V.C. Insulated, Bare Aluminium Sheathed, Aluminium conductor, aluminium sheath, 2- to 3-core, 3/0-29 in. to 19/0-052 in.	4,750
250 and 600 V. Rubber or P.V.C. Insulated, Taped and Braided, Aluminium conductor, single core, 3/0-0.036 in. to 61/0-103 in.	9,500

In addition to the foregoing, some 1,000 yd. of 3-core 0.4 to 0.6 sq. in. paper insulated aluminium sheathed cable having copper conductors has been installed. The decision to employ copper cores in this instance was taken in view of the equivalent conductor size in aluminium, which would have fallen in the range 0.6 to 1.0 sq. in.; in the absence of prior experience some apprehension was felt regarding the handling of such sizes.

For the underground cable, buried direct, the sheath serving consists of overlapped tapes in the order of P.V.C., rubber, P.V.C., hessian. There are bitumen applications over the sheath and over the hessian, which result in a robust finish with excellent water impermeability, and this can be relied upon for complete corrosion protection. The aluminium sheath itself is adequate protection against mechanical damage without the addition of armouring. Within the building, since the

atmosphere is dry and free from corrosive fumes, no sheath protection whatever was thought necessary.

Economic Considerations

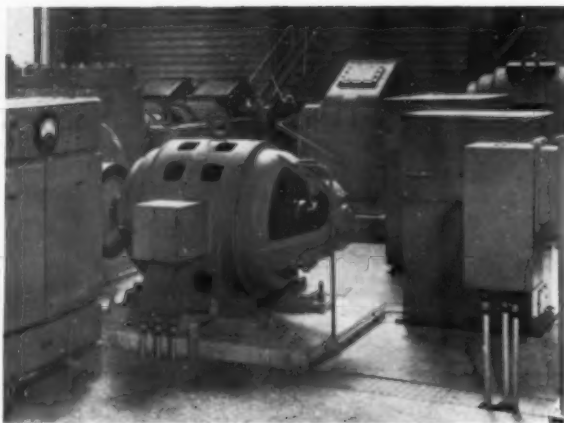
On the basis of 1954 costs, when contracts were placed, the aluminium cable installation showed an overall saving exceeding 6% by comparison with the copper/lead alternative, while in the case of certain individual cable sizes savings up to 25% could be shown. Subsequently, the price differential in favour of aluminium has widened and cost savings resulting from the substitution of aluminium-conductor/aluminium-sheath cables can be claimed, which, today, in certain cases, exceed 33%.

The maximum economic advantage is found in those cables having the largest conductor size and, in considering the overall cost differential of 6% based on 1954 prices, it is important to bear in mind that this was achieved on a factory installation following the usual pattern, in which small cables predominated and larger sizes which showed to maximum economic advantage represented a relatively small proportion of the total cable installed.

Distribution Layout

Power service is established over a 6 kV. ring main from an Area Board sub-station within the works boundary. This ring interconnects the old parent factory sub-station with the new sub-station adjacent to the extrusion plant. This new sub-station in its present stage of development contains three 1,500 kVA., 1 kV/415 V. transformers, together with the high and medium voltage switchgear, and from this point a 6 kV. service to the high tension hydraulic pump motors is taken underground. The aluminium-conductor/aluminium sheath cables for the 6 kV. service were furnished with a protective serving and buried direct.

Medium voltage cables entering the factory from the sub-station have bare aluminium sheaths and pass into the building in an upward direction to the main cable racks situated above crane rail level along the east side. The feeder cables drop vertically to terminal points on



Courtesy of British Insulated Callender's Cables, Ltd.

1,100 V. single-core 0.4 sq. in. aluminium conductor P.I.A.S. cable terminations on 325 h.p. motor.

the east side, or cross the roof trusses to similar terminal points on the west side. Intermediate and final sub-circuit cabling is accommodated on racks along the walls of the building approximately 8 ft. from the floor.

Paper insulated cables with individual loadings from 100 to 1,100 amp. are employed for all outgoing circuits from the sub-station and all main distribution to plant of 60 amp. 3-phase rating and above.

The smaller rubber insulated cables are used for all single-phase circuit distribution and 3-phase sub-circuit wiring for machines, lighting, etc. The larger single aluminium conductor rubber cables are used on single and 3-phase 415 V. circuits for terminations at control panels for heavy-current-consuming furnace equipment. All paper insulated cables are cleated with aluminium alloy claw type cleats and aluminium saddles are used for the aluminium sheathed V.I.R. cables.

Installation of Cables

While aluminium sheaths result in a somewhat more rigid cable than lead sheaths, and hence call for rather more effort for their handling in confined spaces, conventional installation methods proved quite successful. Supports for interior cabling were erected at 4 ft. 2 in. spacing, a distance which it was subsequently found could readily have been increased, though perhaps with some sacrifice of alignment and neatness. The main difference in the use of aluminium as opposed to lead sheathed cables was that rather more time was necessary to straighten the cables for cleating, and to form bends and offsets with a neat and workmanlike appearance, but this was counterbalanced by the distinct advantage of reduced weight. While the size of multi-core all-aluminium cable for this application was limited to 0.3 sq. in., nevertheless the installation demonstrated that all-aluminium power cables substantially larger than this could be satisfactorily installed using conventional practice.

To protect the bare aluminium sheaths from cement where cables pass through walls or floors, two adhesive P.V.C. tapes were applied, each with 50% overlap. When cables were embedded solid in cement, care was taken to ensure that the tape protection was continued well clear of the wall or floor. Apart from this the only special

precaution necessary was to space the bare sheathed cables clear of walls and framing steelwork.

Joints and Terminations

(a) Paper Insulated Cables

Standard techniques and accessories were used with methods of soldering and plumbing already well proved for aluminium cables and which are little different from traditional practice. For conductor joints and terminations the main difference was that within the ferrule or lug the conductor layers were stepped and a special flux (Kynal) was used to remove the oxide layer and to promote good tinning. The solder (Alglo) consisted of a tin/zinc/cadmium/lead alloy.

Briefly the procedure was to heat the conductor by lading solder over it and then to brush the flux vigorously into the strand interstices, followed by alternate applications of flux and solder until complete tinning had been obtained. The ferrule or lug was then placed in position and filled with solder and it should be noted here that the temperature used is no higher than is required when soldering copper conductors. Apart from this soldering operation, jointing practice was normal and the Latchford installation called for approximately 600 soldered ferrules or lugs.

For joints on sheaths the tinning was carried out by rubbing the heated sheath with a stick of tin/zinc or tin/zinc/cadmium solder, following which the plumbing was normal and the accessories entirely standard.

In view of the number of cables entering control gear from above the majority of the cable sealing boxes were top mounted and no sealing compound was used in such terminations. Mass impregnated, non-draining cables were specified and the method employed in sealing the paper insulation was to tape the crutch and conductor tails with three layers of cambrie tape, each layer being varnished after application.

(b) Rubber Insulated Cables

Standard switches and other accessories were used, the only precaution necessary being the liberal application of non-corrosive grease to all mechanical terminations, which totalled more than 3,000.

Lighting Installation

The lighting in the main building comprises triple lamp 5 ft. fluorescent fittings at a mounting height of 30 ft. and at approximately 25 ft. centres. The reflectors are of 20 s.w.g. aluminium alloy, anodised by the sulphuric acid process, and "New Warm White" lamps were installed throughout with a resultant initial light intensity at the working plane of 11 lumens/sq. ft. in the main building, 18 lumens/sq. ft. in the warehouse, and 20 lumens/sq. ft. in the toolroom.

A trunking installation was used for lighting distribution, the fittings themselves being suspended from the trunking by hooks with a plug and socket connection at each lighting source to facilitate removal and interchange either for cleaning or lamp replacement. Lighting wiring comprised 7/0.029 in. single core, aluminium V.I.R. final sub-circuit wiring controlled from wall mounted switchgear served by 7/0.029 in. 4-core aluminium-conductor/aluminium-sheath cable.

The power and lighting installation was carried out by Troughton & Young Ltd., with cables supplied by British Insulated Callender's Cables Ltd. All jointing on paper insulated power cabling was carried out by British Insulated Callender's Construction Co., Ltd.

Sand Mould Penetration Testing

I—A Simple Laboratory Apparatus for Estimating the Resistance of Sand Moulds to Penetration by Molten Metal

By D. H. Houseman, M.A., Ph.D., D. V. Atterton, M.A., Ph.D.,*
and T. P. Hoar, M.A., Ph.D., B.Sc., F.R.I.C., F.I.M.

Department of Metallurgy, University of Cambridge

A simple laboratory apparatus for the measurement of the pressure required to make liquid metal penetrate a sand sample removed from a mould face is described. The preparation of standard sand samples and methods of using the apparatus are described, and some practical results are given and discussed. The apparatus allows an estimation to be made of the degree of ramming in terms of blows of the standard rammer, and also of the maximum metallostatic head that can be supported without penetration occurring.

Introduction

Principle of the Method

THE methods commonly used for testing the efficiency of the ramming of sand moulds, namely, the indentation hardness tester for green moulds and the scratch tester for dry moulds, are somewhat insensitive and, where variations in sand quality are present, may be positively misleading. Moreover, the indentation tester must be used immediately after the ramming of the mould; the surface drying of a mould, even after five minutes exposure to the foundry atmosphere, may be sufficient to give deceptively high readings of mould hardness.

For a sand of uniform quality, the bulk-density gradient method of Davies¹ gives a reliable indication of the degree of compaction that may be attained with a given sand and, if carefully carried out, is free from the defects of the methods just mentioned. It is, however, a test of the sand itself rather than of the actual mould.

We have shown elsewhere² how the method of Davies may be adapted, by the direct removal of a sand sample from the mould face, to give direct readings of "surface" bulk density; the method is, however, slow, some three to four hours being necessary for a single determination. The same paper gives curves relating the degree of ramming (and hence "surface" bulk density) to the penetrating pressure for molten tin and iron—i.e., the metallostatic pressure at the metal/mould interface required to effect metal penetration into the compacted sand.³

We believe that a simple laboratory determination, at room temperature, of the pressure required to make liquid metal penetrate a sand sample removed directly from the mould face (subsequent "patching" of that face being a simple matter), would be a useful addition to routine foundry sand control. The apparatus† described in this paper has been devised for this purpose. A cylindrical sand sample is taken from the mould and

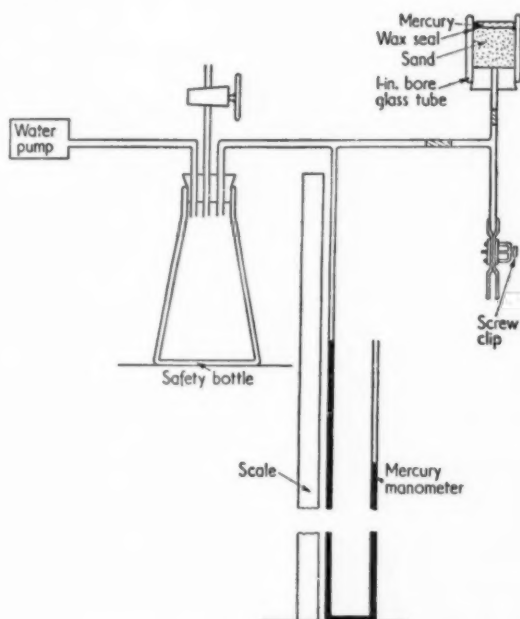


Fig. 1.—Apparatus for the measurement of penetrating pressure (diagrammatic).

sealed into a glass tube; it is covered with a layer of mercury, and the bottom of the tube is connected to a water pump and manometer. Suction is applied, and when mercury penetration is observed, the manometer is read. The penetrating pressure for mercury so obtained may be used directly, by comparison with its values for standard-rammed test compacts, to estimate the degree of ramming of the mould. It may also be converted by simple calculation to give the approximate penetrating pressure for any other metal, and thus the height of that metal that the mould will withstand without allowing penetration.

* Dr. Atterton is now with Foundry Services, Ltd.

† D. H. Houseman and British Steel Castings Research Association, British Provisional Patent Specification No. 8000/53. The apparatus is obtainable from Camlab (Glass), Ltd., Cambridge.



Courtesy of Camlab (Glass), Ltd.

Fig. 2.—The penetration tester.

Experimental Technique

Preparation of Sand Samples

Samples are removed from the mould-face by means of 1 in. diameter cork-borer; the borer is inserted to a depth of c. 1 in., given a slight twist and withdrawn. Since penetration must occur through the surface of the sample, the actual depth of sand removed is unimportant, except that it should be sufficient to prevent any disturbance of the surface layers of sand when the sample is pushed out (from the bottom) by means of a stripping post. Samples may be collected on a wooden tray having 1½ in. diameter holes numbered to facilitate identification; they are then dried in an oven at 120° C. for 30–40 minutes and allowed to cool.

Standard samples of compacted sand are similarly prepared, for comparison purposes, by ramming standard (2 in. diameter, 2 in. high) A.F.A. test pieces and using the cork borer to remove 1 in. diameter cylindrical samples from the test pieces while they are still in the ramming tube. Usually six standard samples, made with ¼, 1, 2, 3, 6 and 10 standard rams, are sufficient to determine the course of a penetrating-pressure/degree-of-ramming curve.

Design and Operation of Penetration Tester

The apparatus is shown diagrammatically in Fig. 1, and as manufactured in Fig. 2.

A dried sample is placed in the cylindrical tube with the mould-face end upwards, and carefully sealed round the edges with paraffin wax kept at 80–100° C. above its softening point and applied by means of a small brush. A seal to c. ¼ in. depth down the cylindrical surface of the compact should be aimed at in order to give a strong wax layer and to prevent mercury breaking through to give false readings; this can only be achieved if the wax is sufficiently hot.

The prepared sand sample is covered by a layer of mercury from the reservoir; contact probes of an elec-

trical circuit are used to indicate a standard depth of mercury of 0.5 cm. by means of a small lamp and/or a buzzer. A pressure difference across the mercury layer is then built up by evacuating the apparatus by means of a water pump; when this pressure difference becomes great enough for penetration of the compacted sand by the mercury to occur, the electrical circuit is broken, and the pressure difference is at once read on the manometer. The mercury quickly penetrates completely when the penetrating pressure has been reached and is recovered by opening a screw clip.

Pure mercury cannot be used in the penetration tester, since increasing contamination of the mercury during use alters its surface tension and the contact angle it makes with sand, and thus gives values of penetrating pressure that cannot be properly compared. Mercury is therefore conditioned before use by being sucked repeatedly through a bentonite-bonded sand compact until contamination by the materials of the compact has produced a steady value; reproducible and comparable readings are then obtained.

Experimental Results

Reproducibility Tests

A coarse sand mix of composition

Leighton Buzzard sand (Arnold's 52A)	..	92 wt. %
Quest bentonite	..	4 wt. %
Water	..	4 wt. %

was made in the laboratory with a Simpson 20 lb. mill (Sand Mix I). A series of sample compacts given 10 standard rams was made from it and tested for reproducibility, with the results shown in Table I.

TABLE I.—REPRODUCIBILITY TESTS.

Exp. No.	Penetrating Pressure (cm. Hg.)	Remarks
1	6.3	
2	5.9	
3	6.5	
4	4.5	Leak through wax seal
5	6.6	
6	6.4	
Mean	6.4	Exp. 4 omitted

The error in any individual determination may be ± 0.2 cm., so that reproducibility to ± 0.5 cm.—the same as that obtained with the higher-temperature tin and iron experiments that we have previously reported²—is obtainable. As Experiment 4 of Table I indicates, a faulty experiment leads to a low reading, so that a well-rammed mould area might be identified as "soft" (and given more ramming); but a soft area that might give penetration trouble could never be identified as being satisfactorily hard. Indentation testers, on the other hand, tend to read "over hard" when in error, as shown below.

Comparison of Penetration Test and Green Hardness (Indentation) Test

A typical steel-foundry facing sand mix of composition

Erith sand	..	92.2 wt. %
N. African bentonite	..	4.2 wt. %
Cereal binder	..	0.9 wt. %
Water	..	2.7 wt. %

was made in the foundry (Sand Mix II). Four series of A.F.A. standard-rammed test pieces were prepared from it with ¼, 1, 3 and 10 standard rams. The hardness of one piece from each series was determined at six points on the rammed face immediately after ramming with an

* "¼-ram" test pieces are made by allowing the rammer to fall through 1 in. instead of 2 in.

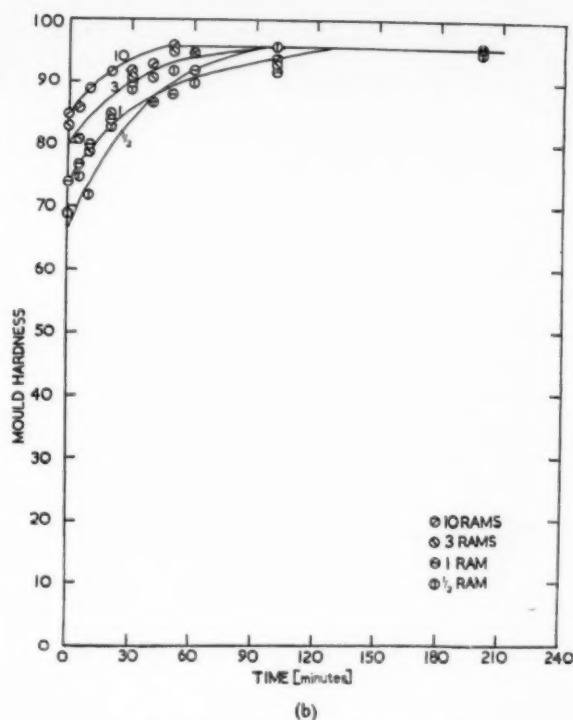
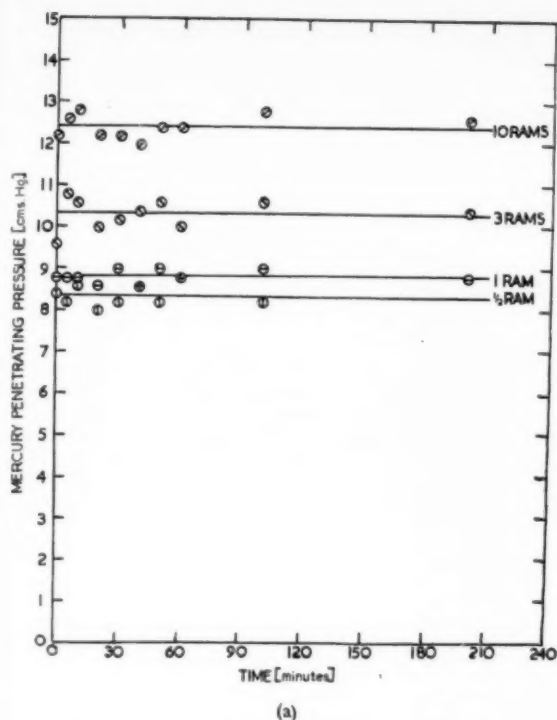


Fig. 3.—Comparison of (a) penetration and (b) indentation tests on fresh and partially air-dried samples.

indentation tester of the type due to Dietert, and a 1-in. diameter sample from the middle of the rammed face was removed, dried at 120°C. for 30 minutes, and tested for mercury penetration. Both tests were repeated on other test-pieces that had been allowed to dry partially in the laboratory atmosphere at 19°C. for various periods. The results are shown in full in Table II and Fig. 3 (a) and (b).

It may be seen that both tests, when made on test-pieces immediately after ramming, placed the differently

rammed test pieces in the correct order, but that the penetration test indicated a greater relative difference between them, in much better agreement with the relative behaviour of soft- and hard-rammed sand in practice. Furthermore, the hardness test distinguished properly between the test pieces only when it was carried out immediately after ramming, or after a rather short (and constant) interval. The penetration test, however, being made on dried-out specimens, gave the same result whether the sample for it was taken

TABLE II.—MOULD HARDNESS AND PENETRATING PRESSURE VALUES FOR AIR DRIED A.F.A. STANDARD RAMMED TEST PIECES.

Time after Ramming (min.)	1/2 Ram			1 Ram			3 Rams			10 Rams		
	Mould Hardness		Mercury Penetrating Pressure (cm. Hg.)	Mould Hardness		Mercury Penetrating Pressure (cm. Hg.)	Mould Hardness		Mercury Penetrating Pressure (cm. Hg.)	Mould Hardness		Mercury Penetrating Pressure (cm. Hg.)
	Actual Readings	Mean		Actual Readings	Mean		Actual Readings	Mean		Actual Readings	Mean	
0	78, 75, 71, 66, 64, 61	69	8.4	80, 79, 76, 69, 69, 69	74	8.8	88, 84, 83, 83, 83, 79	83	9.6	90, 88, 86, 83, 82, 82	85	12.2
5	82, 75, 75, 75, 73, 72	75	8.2	80, 79, 78, 78, 76, 72	77	8.8	85, 84, 82, 80, 78, 75	81	10.8	89, 88, 88, 85, 85, 82	86	12.6
10	80, 77, 76, 74, 66, 60	72	8.6	84, 82, 81, 81, 80, 75	80	8.8	84, 82, 80, 79, 77, 74	79	10.6	92, 90, 89, 89, 87, 86	89	12.8
20	87, 85, 83, 82, 81, 78	83	8.0	89, 88, 87, 87, 81, 75	84	8.6	89, 88, 88, 87, 82, 78	85	10.0	94, 92, 92, 91, 91, 91	92	12.2
30	92, 91, 91, 89, 86, 84	89	8.2	92, 92, 91, 89, 89, 88	90	9.0	93, 93, 92, 91, 91, 88	91	10.2	94, 93, 93, 92, 91, 90	92	12.2
40	91, 89, 88, 87, 86, 83	87	8.6	91, 91, 87, 86, 85, 85	87	8.6	93, 92, 91, 90, 90, 88	91	10.4	95, 94, 94, 93, 92, 92	93	13.0
50	98, 94, 92, 91, 89, 89	92	8.2	94, 90, 87, 86, 86, 86	88	9.0	96, 96, 96, 96, 95, 93	95	10.6	98, 97, 97, 96, 95, 95	96	12.4
60	94, 95, 91, 90, 89, 85	90	8.8	94, 94, 94, 93, 90, 89	92	8.8	95, 95, 95, 95, 94, 94	95	10.0	95, 95, 95, 95, 94, 94	95	12.4
80	97, 97, 96, 96, 96, 94	96	8.2	94, 93, 93, 92, 92, 90	92	9.0	95, 94, 93, 93, 92, 92	93	10.6	98, 96, 94, 94, 92, 91	94	12.8
90	99, 96, 95, 94, 94, 93	95	—	98, 98, 97, 96, 94, 93	96	8.8	98, 98, 97, 96, 95, 93	96	10.4	98, 97, 96, 96, 95, 92	96	12.6

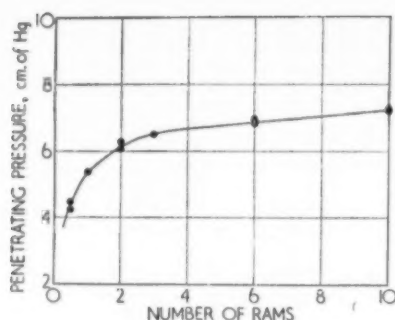


Fig. 4.—Penetration pressure for mercury vs degree of ramming.

immediately after ramming or after any interval up to 200 minutes, during which the tested surface has become partially air-dried.

In practice it is usually impossible to conduct hardness tests at various parts of a mould immediately after ramming or after a short constant interval. There seems to be little reason, however, why penetration-test samples should not be taken relatively at leisure; and the above results show that they should give strictly comparable penetrating pressure readings, independent of the interval between ramming and sampling.

Application to a Foundry Sand Mix

In using the penetration tester with a given foundry mix, a series of standard-rammed test pieces is prepared in duplicate or triplicate and tested to establish the penetrating-pressure/degree-of-ramming curve. A foundry sand mix of composition

Leighton Buzzard sand (Arnold's 52A)	92.6 wt. %
Quest bentonite	3.7 wt. %
Water	3.7 wt. %

was prepared as a 500 lb. batch in a Foundry Equipment S.B.2 mill (Sand Mix III), for making the hand-rammed mould described in Part II of this series of papers. This mix is as coarse as is ever ordinarily used in foundry; it leads to low penetrating pressures, and the effects of poor reproducibility are at a maximum. Nevertheless, a very satisfactory duplication of certain points in the penetrating-pressure/degree-of-ramming plot is shown in Fig. 4, and the curve through all the points is smooth. Over the range $\frac{1}{2}$ –10 rams the penetrating pressure increased by c. 65%, and thus by determining the penetrating pressure of samples removed from moulds made up from this mix, the degree of ramming at the regions sampled could be estimated, as described in Part II.

Estimation of Maximum Head of Metal that a Mould will Withstand

The penetrating pressure for the tested mould with "conditioned" mercury, as determined by the present apparatus, is directly proportional to the maximum head of any other molten metal that the mould will withstand (at the region tested) without penetration. For any metal, the penetrating pressure p dynes/sq. cm. is given by

$$p = - \frac{2\sigma \cos \theta}{r}$$

where σ dynes/cm. is the metal surface tension, θ is the contact angle of the metal with the mould material and

r cm. is the effective pore radius,³ under the conditions obtaining. Consequently the height h cm. of metal that will stand on the mould is given by

$$h = - \frac{2\sigma \cos \theta}{g\rho r}$$

where g is the acceleration due to gravity and ρ g./c.c. is the metal density. Thus, if the suffix Hg denotes the values of the variables for mercury under the conditions of the mercury-penetration test,

$$h = \frac{\sigma \cos \theta}{\rho r} \cdot \frac{\rho_{Hg} r_{Hg}}{\sigma_{Hg} \cos \theta_{Hg}} \cdot h_{Hg} = Ah_{Hg},$$

where A is a factor depending on the metal and mercury surface tensions, contact angles and densities, and also on the effective pore radii of the mould-face sample used in the mercury test and of the mould under casting conditions.

Little sand sintering occurs at temperatures up to 1,400° C. and the effective pore radius r remains constant and equal to r_{Hg} ; thus for non-ferrous metals and (probably) cast iron, A depends entirely on the metal properties. For steel and pure iron, however, the higher pouring temperatures lead to an increase of effective pore radius^{2,3} and to a decrease in A .

Approximate calculations of A can be made from the approximately known values of the surface tensions, contact angles and densities, and (where necessary) from the change of effective pore radius caused by sintering (as determined by methods that we have reported elsewhere).² However, it is more satisfactory to determine A by direct experiment, that is, by measuring h for a given compacted sand by means of either a laboratory or a foundry high-temperature experiment with the metal concerned, and h_{Hg} by means of the penetration-tester technique. Once A for a given sand mix has been thus found, mercury-penetration results on a mould made from that mix can at once be converted to give maximum heights of metal that the mould will withstand. Furthermore, A is substantially unchanged for other sand mixes, and can thus be used for them also, provided that sintering is substantially absent, as will usually be the case in non-ferrous and probably cast-iron founding. Since, however, different mixes sinter to different extents above c. 1,400° C., leading to different changes of r , A must be determined for each mix if it is used for estimating h in steel founding; also, the estimation will be accurate only for a particular pouring temperature and for a particular period during which metal is molten at the metal/mould interface, since sintering is increased by increase of temperature and is progressive with time. Nevertheless, a reasonably good value of A for general use in a particular steel foundry is doubtless obtainable from relatively few trials, and thereafter values of h quite accurate enough for practical use could be found directly from mercury-penetration results.

Some examples of the values found for A may be of interest. The penetrating pressure, for mercury, into the above-described Sand Mix I compacted to 10 rams was 6.3 cm. of Hg (Table I). A 10-ram compact of the same sand was tested in the high temperature apparatus that we have described elsewhere^{2,3} for penetration by tin at 650° C., *in vacuo*. Penetration occurred at a pressure of 12.0 cm. of Hg, equivalent to a height of 23.4 cm. of tin; this leads to a value of A of $23.4/6.3 =$

3.7 for tin, and since there can be no sintering at 650° C., it is likely that this value would be little altered with other sand mixes.

10-ram compacts of Sand Mix I, inserted into the mould described above, were tested for penetration during the making of the low-carbon steel casting at 1,530° C., under ordinary atmospheric conditions. The steel was poured at a temperature of only a few ° C. above its liquidus, and the metal in contact with the mould surface was molten for c. 50 seconds. Penetration occurred under a head of 58 ± 3 cm. of steel; this leads to a value for A of $58/6.3 = 9.2$, which probably represents about the highest value attainable with steel by careful pouring practice designed to minimise sintering.

As an example of severer conditions, a similar 10-ram compact was tested for penetration by iron at 1,600° C. (65° C. above the liquidus) after molten metal had been in contact with the rammed-face for c. 75 seconds, *in vacuo*. Penetration occurred at a pressure equivalent to 50 ± 1 cm. of iron, which leads to a value for A of 8.0 for these conditions where sintering is considerable.

In general it may be said that when sintering occurs, the highest values of A are obtainable by pouring at low temperatures and by designing castings so that the metal at the metal/mould interface is molten for as short a time as possible. Probably a value of 8 can be taken as a conservative one for normal steel-founding practice, but, as pointed out above, direct determination for particular conditions is always desirable.

Summarized Conclusions

(1) Apparatus of simple design is described whereby a sample may be removed from the face of a sand mould or

standard compact and tested for its resistance to penetration by mercury at room temperature. The pressure required to make mercury penetrate is directly measured.

(2) The degree of ramming of the mould face can be estimated by comparison of the results obtained on mould samples and on samples from test compacts made with standard degrees of ramming. The results are more consistent than those obtainable by green hardness (indentation) measurements.

(3) The height of molten metal that a given mould will withstand without penetration can be estimated from mercury-penetration test results by mean of a conversion factor. This factor can be established by comparison of mercury penetration pressure with laboratory or foundry determination of the penetrating pressures needed to force the molten metal into similar compacted sand under casting conditions. The factor is 8.9 for steel at steel-founding temperatures, depending on the degree of sintering of the mould.

Acknowledgments

This work is part of a general programme on steel-casting defects, financially supported by the British Steel Castings Research Association, that is being conducted in the Department of Metallurgy, Cambridge University. We are greatly indebted to the Association and its officers for their continual help.

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Gear Hardening by Drip Feed Technique

New Furnace Installation at Vickers-Armstrongs (Engineers), Ltd.

NEW electric furnaces recently installed at the Elswick and Scotswood Works of Vickers-Armstrongs (Engineers), Ltd., include two batch furnaces with separate cooling chambers—for gas carburising gear wheels—and a continuous hardening furnace with a roller hearth. The processing atmospheres are generated within the furnaces from a liquid mixture introduced by a drip feed technique. The furnaces were designed and supplied by The General Electric Co., Ltd., which also developed the special fluid from which the atmospheres are obtained.

Carburising Plant

The carburising furnaces are of identical design, each having a set of three baskets to carry the charge, with effective dimensions 25 in. in diameter and 36 in. deep. Inside each furnace is a heat-resisting steel lining, which is supported by a wide flange and is free to expand at the base with the increase in temperature. Round the outer periphery of the chamber is a sand channel which takes the furnace lid to effect a gas tight seal, whilst the bottom of the chamber extends into an oil sealing trough. Each furnace is closed by an easily operated lift-and-swing lid having a leaf spring and a ratchet-operated lifting lever. The lids, which are lined on the inside

with heat-resisting steel plate, are centrally supported and can be rotated with tommy bars for bedding down in the sand seals.

The carburising fluid is pumped to each furnace from its own storage tank, and injected through an inlet in the



Batch type gas carburising furnace and cooling chamber.



A gear being removed from the roller hearth furnace for quenching.

lid. It drips on to a hot plate within the furnace chamber where it volatilises. The atmosphere generated in this way is circulated rapidly round the charge by a centrifugal impeller, situated beneath the stool which carries the baskets, with its blades operating within the chamber.

The furnace elements are of heavy gauge nickel-chrome ribbon carried on the inner furnace lining and protected by the steel lining or chamber from the carburising atmosphere: each furnace has a maximum rating of 90 kW. The cooling chambers are of the same size and shape as the furnace chambers and are sealed in the same way with lift-and-swing type lids engaging in sand channels.

For partially cooling the gear wheels before transferring them to a cooling chamber, air can be admitted through

portholes in the lower part of the furnace walls and allowed to circulate round the outside of the carburising chamber. The gears are supported for carburising on suitable jigs, in order to minimise or eliminate distortion, and are placed in the furnaces in baskets of heat resisting steel.

Hardening Furnace

The carburised gear wheels are subsequently case hardened by heating in the roller hearth furnace and quenching in oil under a press. The gears are inserted into the furnace on trays and are moved continuously along by the rollers, which are driven by an induction motor through reduction gears. The time taken for the gears to pass through the furnace can be varied from 31 to 155 minutes, the actual time being shown on a tachometer mounted near the drive unit. As a charge approaches the exit end it breaks a beam of light falling on to a photo-electric cell, and an alarm bell rings to warn the operator that a charge is ready to be removed. The doors at both ends of the furnace are suitably counter-balanced, and are operated hydraulically with foot controls. Cradles and idle rollers are provided to facilitate loading and unloading.

The furnace has a heated length of 15 ft. and a maximum rating of 100 kW. The elements, which are constructed from heavy gauge nickel-chrome ribbon, are mounted in the roof and in the hearth: they are arranged in two independently controlled zones. During the time that the gears are in the furnace they are protected from scaling by an atmosphere generated from a fluid introduced by the drip feed technique through inlets in the furnace roof.

Both the gas carburising furnaces and the roller hearth furnace provide for temperatures up to 1,000°C., and are fitted with automatic temperature control and recording gear.

Swaziland Coal and Iron Deposits

In the recently published White Paper (Cmd. 9580) on economic development and social services in the High Commission Territories, a brief reference was made to the existence of iron ore and coal deposits in Swaziland. Although investigation of these deposits will not be completed until 1957, the Geological Survey Department of Swaziland has produced an interim memorandum for the information of any person who may be interested in acquiring the mining rights.

The main iron ore deposit, located at Bomvu Ridge near Darkton in North West Swaziland, consists of a high grade haematite with an indicated grade of 64% iron and 3.5% silica. Reserves are estimated at between 40 and 50 million tons. There are also deposits of low grade ore in South Swaziland, but these are unlikely to be exploited at present. The coal deposits form a north-south belt in Eastern Swaziland 80 miles long by 5 miles wide, and have been geologically mapped by the Geological Survey Department.

Mining rights in Crown Mineral Areas, in which the Bomvu Ridge iron deposits and certain of the coal deposits are located, may be granted, on application, by a Special Authority issued by the Resident Commissioner, Swaziland. Where coal deposits are located on mineral concessions, applications for mining rights should be sent to the concessionaires. New mining legislation is at present under consideration, and if

approved will have the effect of facilitating the acquisition of mining rights in mineral concession areas.

A complementary investigation into the possibility of developing hydro-electro power from the Great Usuto River is going on at present. It is hoped that a report will be issued in the near future. At present all transport in the Territory is by road, but the whole system of communications is being investigated in detail.

Welding Courses for Overseas Students

EVERY year a number of students visit this country from overseas to take courses in welding and cutting. They come from countries as far distant as Egypt, Nigeria, the West Indies, the Gold Coast, India and Pakistan. By the end of the year, about a dozen of these students had passed through the British Oxygen Company's school at Cricklewood, London. They take courses varying from two weeks to three months, but they normally spend a much longer period in this country, as the expense of travelling from overseas would not be justified for a course which lasted only a few weeks. Most of the students are sent over either by the Government or the company which employs them. About one-quarter of the students who go to Cricklewood are sent there from British Oxygen's overseas companies.

Henry Cort

Wrought Iron Pioneer

By Eric N. Simons



THE precise character of Henry Cort's contribution to the progress of metallurgy is not wholly a matter of common agreement. Some regard him as an originator of the first rank, whose discoveries were of enormous importance. Others consider him merely a plagiarizer or borrower of the ideas of others, improving upon them with results admitted to be beneficial. Whichever view is taken, however, he is important.

Born in 1740 at Lancaster, Cort was the son of a builder and brickmaker. Virtually nothing is known of his early years, but by his own industry and perseverance, he seems to have raised himself to a position of some standing, because in 1765 he is found in business as a Navy agent in Surrey Street, Strand, London. He appears to have prospered in this business, in the course of which he saw that foreign iron was much superior to that supplied by the British manufacturers. In fact, the English wrought iron was so poor that the Government would not allow it to be used by the Navy, while the cast iron was so brittle that it was of little use even for general purposes.

Cort wished to provide the Navy with better iron, whether from patriotism or self-interest cannot be said. His experience of metallurgical operations can only have been slight, nevertheless he began to experiment. The scope and form of his experiments is unknown, and the only trustworthy data are that in 1775 he threw up his Navy agency and rented a piece of land at Fontley, near Fareham, in the Portsmouth region. Here he built a forge and an iron mill, taking at the same time a partner named Samuel Jellicoe (son of Adam Jellicoe, deputy paymaster of seaman's wages).

Earlier Work

In discussing Cort, we must remember that in various directions he had certainly been preceded by earlier inventors. For example, in 1728 Payn and Hanbury had designed a mill for rolling sheet iron. In 1766, nine years before Cort set up his works at Fontley, the

brothers Craneage had adopted the reverberatory or air furnace, in which they placed the pig- or cast-iron, and without a blast or any fuel other than ordinary raw pit coal, converted it into good malleable iron. This iron, taken red-hot from furnace to forge hammer, was then drawn into bars.

In the same year as that in which Cort first published his patents, Peter Onions, of Merthyr Tydvil, developed another process of iron manufacture, in which, using a furnace "bound with ironwork and well annealed," he charged it with pig- or fused-cast-iron from the smelting furnace. The furnace was then sealed and the doors luted with sand. The fire was invigorated by a blast admitted underneath, probably to maintain combustion of the fuel on the grate. Onions's furnace must have resembled the modern "puddling" furnace, which also employs a blast. The fire had to be maintained until the metal lost fluidity and "thickened into a kind of froth, which the workmen by opening the door must turn and stir with a bar or other iron instrument, and then close the aperture again, applying the blast and fire until there was a ferment in the metal." The patent further describes that "as the workman stirs the metal" the scoriae will separate "and the particles of iron will adhere, which particles the workmen must collect or gather into a mass or lump." This mass then had to be brought to a white heat and forged into malleable iron at the forge hammer.

Cort's own patents were published in 1783 and 1784, at once establishing a new metallurgical era. He himself said: "after great study, labour and expense in trying a variety of experiments, and making many discoveries, I have invented and brought to perfection a peculiar method and process of preparing, welding and working various sorts of iron, and of reducing the same into uses by machinery: a furnace and other apparatus adapted and applied to the said process." Although Cort has been accused of pirating Onions's idea, it is more likely that the appearance of his patents so soon after Onions's own

was a coincidence. Watt, in his letters to Boulton, describes Cort as "a simple, good-natured man," which does not suggest a shameless exploiter of his fellows. He may, however, have had some inkling of the ideas of the brothers Craneage.

The object of Cort's process was to convert cast or pig-iron into malleable iron by the flame of pit coal in a common air-furnace, and to form the result into bars by using rollers instead of hammers. He made at Fontley iron that could be used for large pieces, such as shanks, arms, rings and palms of anchors. This he did by the method of piling and faggoting, i.e., by laying bars of iron of proper lengths, specially forged, and tapering, so as to be thinner at one end than the other, in the manner of bricks in buildings. The faggots, to the amount of half a ton or less, were put in a common air or balling furnace, and brought to a welding heat in a much shorter time than in any hollow fire. When the heat was perfect, the faggots were brought under a forge hammer of great size and weight (for those times), and welded to a solid mass. He also worked the faggots by passing them through grooved rollers.

Although Cort did not invent rolls for this purpose, little use had been made of them until he introduced his new method. The smallest size drawn under the hammer at that time was $\frac{3}{4}$ in. square, below which everything had to be cut in a splitting mill. The hammer had to be kept continually at work to draw a mere ton of average sizes in 12 hours. With Cort's rollers, 15 tons could be made in the same time with one pair of rollers and 5 tons of the small sizes in 12 hours.

Improved Process and Product

Cort's second patent covered a method of making bar iron from ore and cast iron, using the reverberatory furnace without blast and working the fused metal with iron bars, until it had been brought to lumps. It was then removed and forged into malleable iron. Cort did not invent the reverberatory furnace, but improved the process in the following ways.

The bottom of the furnace was made hollow to contain the liquid metal poured into it by ladles, pit coal or other fuel used for firing. When the furnace was charged, the doors were closed until fusion of the metal was adequate, whereupon the aperture was opened and the iron stirred with iron bars, producing an ebullition. A bluish flame was emitted, the carbon of the cast iron was burned off, the metal separated from the slag, and the iron, being reduced to nature, was then collected into lumps or loops of sizes suitable for the purposes to which it was to be put. These were then drawn out of the doors of the furnace, stamped into plates, and piled or worked in an air-furnace, heated to a white or welding heat, shingled under a forge hammer, and passed through the grooved rollers.

On hearing of Cort's remarkable improvements, a number of iron masters visited his works, and in 1787, Richard Crawshaw, of Cyfartha contracted with him to work under his patents at 10s. a ton royalty. The quality of Cort's iron was so good that the previous Government prohibition was revoked, his iron being specified as suitable for the ships of the Royal Navy. In 1792, Newton Chambers, of the Thorncroft Ironworks, Chapelton, nr. Sheffield, made iron by Cort's process. Even earlier (1789) the Low Moor Ironworks, near Bradford, did the same, as did Dobson and Barlow, of

Bolton, in 1790. In 1803 the works at Low Moor installed one of Cort's puddling furnaces.

Cort now hired a wharf at Gosport belonging to his partner's father, and was successful in obtaining orders for iron from the British Government, producing a considerable tonnage for the period.

Misfortune Strikes

A tragic event marred Cort's life, when Adam Jellicoe, his partner's father, died. A few days before his death a thorough investigation of his accounts had been instituted, and it was found that he had defrauded the public, to the tune of roughly £40,000. Documentary evidence proved that all and more had been spent by him in financing Cort's experiments. Jellicoe's estate was owed altogether £90,000, £55,000 of this by Henry Cort. At first sight it might seem as if Cort had connived at Jellicoe's defalcations, but there is not the slightest proof of this, nor any reason to believe that Cort knew of or suspected the source of his backer's money. (Which of us in similar circumstances would ask questions?) To Cort, Jellicoe was, as he was to others, a rich man, and, one assumes, a man unlikely to admit to others that he had achieved wealth by speculation.

Of the £47,000 of which he had robbed the public, it was clearly shown that £27,500 of this had been handed over to the ironfounder instead of being used, as it should have been, to pay the wages of seamen and officers. Despite lack of evidence of complicity between Cort and Jellicoe, Cort's estate was commandeered by the Government to secure repayment of as much as possible of his debt to the dead man.

Then occurred one of the grossest examples of injustice and stupidity for which a British Government has ever been responsible. Instead of allowing Cort to carry on running his works and using his patents under Government supervision, so enabling him to pay off by degrees the money owing, which would have taken only a few years at most, the arbitrary step was taken of putting, of all people, his partner, Samuel Jellicoe, in possession of Fontley and Gosport. Cort was excluded from his own works for a period of no fewer than 14 years.

It must be noted that, on receiving the advance from Adam Jellicoe, Cort had made over his patents to him in return, and the Government took over the assignments of these. Their folly and mismanagement will be appreciated when it is known that the assignees *never levied a single patent right*, so that the advantages derived from the inventions of Cort were practically handed over free of charge to the iron-masters and the public. In effect the Cort estate produced only the relatively small sum of £2,654, whereas properly managed and with patent rights fully levied, it could have been made to wipe out the entire debt. To indicate how little business sense was brought to this question, it may be mentioned that in the Report of the Commission of Naval Enquiry (1805), the value of Cort's patents was estimated at £100.

The net result of these blunders was not only the loss to the Treasury of a considerable sum of money, but also the bankruptcy and destitution of the inventor himself, left with a wife and twelve children on his hands. From correspondence preserved, it is known that James Watt was sympathetic, doing all he could to assist his fellow-inventor. In 1794, a number of Members of Parliament petitioned Pitt, the Prime Minister, as a result of which Cort was granted a pension of £200 a year. This was barely enough to keep the family in good health, and it

is not surprising that in 1800 Henry Cort died, broken in health, at the age of sixty. He was buried in the churchyard at Hampstead.

In 1802 his widow was granted a pension of £125, but she could not keep her numerous family on so small a sum. In 1811, therefore, an appeal was made to all those ironmasters who had benefited by Cort's improvements to contribute voluntarily to a fund for her benefit. It is a significant commentary on the character of those who are known to have made many thousands of pounds out of the dead inventor's processes that the fund, when closed, had realized a total of only £870, representing the contributions from the ironmasters of the entire Kingdom.

Summing up the work Cort did for iron manufacture, it may be said that he greatly simplified the conversion of cast iron into wrought iron. His reverberatory

puddling furnace enabled the iron to be kept in a chamber separate from the fire, which thus removed it from the carburizing influence of the fuel, although it was heated by the flame which the fuel itself emitted. In the old type of forge there was close contact between the iron and the fuel, and as the fuel was itself an active carburizing agent, decarburization was very difficult.

The photograph of Cort reproduced here is a fine impression of a mezzotint portrait, presented to the Iron and Steel Exchange by Mr. Walter Barnard in 1928 or 1929. It carries a plaque reading: "To the Iron Trade of Great Britain this Portrait of the late Henry Cort, the Tubal Cain of our Century and of our Country, 'the Father of the British Iron Trade'—*Times*, July 29th, 1856, is respectfully dedicated by his obedient Set.—Richd. Cort."

Centenary of "The Engineer"

RARELY do we have the opportunity of congratulating a contemporary on the occasion of its centenary, but we take pleasure in offering our felicitations to *The Engineer* whose first issue appeared just over a hundred years ago—on January 4th, 1856, to be precise. Of the journals devoted, wholly or in part, to engineering, which were in existence at that time, only four have survived to the present day, and only one—*Mechanics* (formerly *Mechanics Magazine*)—covered engineering as a whole. Judged by early issues, *The Engineer* seems to have been founded with the idea of giving publicity to the spate of inventions being patented in the fifties of the last century—indeed, reference was made in a leader of 1858 to the job of *The Engineer* as . . . "to teach the young idea to shoot so as not to miss the mark which should be aimed at, namely, the utilisation of inventions." Some years later the policy was changed for that of describing the actual products of engineering manufacture, and of giving space to the publication of technical and theoretical articles contributed by notable engineers of the day.

Many old-established firms have flourished under the guidance of successive generations of a single family. What is remarkable and probably unique in the history of *The Engineer* is that three generations of each of three families have co-operated, each in their own sphere, towards making the journal a success. *The Engineer* was founded by Edward Charles Healey in 1856: since then, without a break, the head of the firm has always been a Healey. Edward was succeeded by his son, Sir Charles Chadwyck-Healey, Bt., who in turn was followed by his son, Sir Gerald. The present chairman is Mr. Oliver Chadwyck-Healey, brother to Sir Gerald. On the editorial side, the present editor, who succeeded his father in 1946, is a grandson of Vaughan Pendred, who occupied the editorial chair from 1865 to 1905. Three generations of that family have, therefore, edited the journal over a span of 90 years. The family influence extends to the printers. George Reveirs, who founded the printing firm of George Reveirs, Ltd., in 1874, was responsible as a member of the composing room staff of Samuel Taylor of Greystoke Place, a firm he eventually took over, for composing the original prospectus heralding the advent of *The Engineer*, and his firm, of which his grandson George Leopold is still a director, has printed the journal ever since.

To commemorate the occasion, a special Centenary Number has been produced, of a format very similar to that of ordinary issues, but containing 452 pages. The 124 editorial pages open with a short history of the journal, which is followed by four pages of reproductions of engravings which appeared in early issues, and which reveal both the skill and the artistry of old time engravers. One of them, representing the Great Westminster Clock (Big Ben) was not, we understand, known by horologists to exist. It is of special interest because it will reveal to them what they have long wished to know, what this clock mechanism looked like in its maker's works for the four years during which it remained there before installation in the tower.

Most of the rest of the Centenary Number—by far the greater part of its editorial contents—is devoted to the presentation of a group of 26 articles, contributed by eminent men and all gathered under the general title: "A Study of Influences on Engineering Advancement, 1856-1956." In Part I, "The State of the Art and Science in 1856" is discussed; in Part II, "Basic Influences"; in Part III, "The Influence of Engineering Discoveries"; in Part IV, "The Influence of Production Methods"; and in Part V, "Governmental and Similar Influences." There then follows a section in which a number of modern engineering products are illustrated in colour, and the editorial concludes with a list of 147 manufacturing and consultant firms, 12 institutions and societies, and four technical journals that were all founded before the first issue of *The Engineer* appeared.

Pig Iron Prices

THE Iron and Steel Board have announced increases in the prices of basic pig iron, hematite pig iron, low phosphorus foundry iron and Scotch foundry iron. These changes are necessary to take some account of the higher cost of ore, in particular the increase in the cost of ocean freight of imported ore. The increases in basic prices are: basic pig iron—11s. 6d. a ton; hematite pig iron—17s. 6d. a ton; low phosphorus foundry iron—16s. a ton; and Scotch foundry iron—7s. 6d. a ton. There are also increases in the extras for low phosphorus, and high silicon and manganese contents. No changes are at present being made in the maximum prices of steel products determined by the Board.

Correspondence

THE HEAT RESISTANCE AND APPLICATIONS OF HOT DIP ALUMINISED STEEL

The Editor, METALLURGIA.

Sir,

It will be realised from Dr. Hughes' reference to this Company in the introductory section of the above paper that we have been in fairly close touch with the general trend of the work described. We should appreciate the opportunity of making one or two additional comments with reference to the behaviour of sprayed coatings in service at high temperature.

(1) It is not the practice to recommend the use of aluminium coatings in the as-sprayed condition at temperatures above 550°C.,¹ and specimens of this type of coating were included in these tests merely for the sake of comparison.

(2) The heat treated sprayed aluminium coating known to the metal spraying industry for many years as aluminising is used for service conditions above 550°C., and it is the iron-aluminium alloy layer resulting from diffusion heat treatment that provides the protection against high temperature oxidation. From this it will be realised that hot dip aluminised coatings are more comparable with these sprayed and heat treated coatings than with the coatings in the as-sprayed condition. The main distinction between the two types of aluminised coating lies in appearance and thickness. The dipped coatings are in general thinner and brighter. Basically, their protective ability is similar, allowing for differences in life expectancy due to thickness, and they are of similar constitution.

(3) The greater weight gains shown in Figs. 2b and 3b are to be expected in view of the comment made in (1), above, and can be explained in the case of the heat treated deposit on the basis of the larger surface area associated with deposits produced by spraying. The surface area effect remains even after the diffusion heat treatment. Furthermore, it must be remembered that evidence based entirely on weight changes does not give a complete picture of the protection given to the basis metal.

(4) Finally, a word of explanation is due with reference to the alloy sprayed deposits mentioned in the paper.

The aluminium-5% silicon coatings are not sprayed in commercial practice by this Company for any applications connected with corrosion or high temperature oxidation. They were produced for this experimental work: (a) to determine whether there would be any preservation of appearance such as is obtained with the hot dip aluminised coating when the bath contains silicon; and (b) to investigate the resistance of diffusion heat treated deposits produced from this alloy, compared with the usual type of aluminising carried out by the metal spraying industry. No advantage from either of these sources has been derived from the use of this alloy in any condition. The as-sprayed aluminium-silicon alloy was again merely included for the sake of comparison.

Reference has been made in the paper to sprayed coatings containing cadmium. These are the (sprayed) aluminised coatings produced in commercial practice by the heat treatment of a sprayed coating deposited from

a wire containing 0.5%-0.75% cadmium, and its function is to prevent oxidation during diffusion heat treatment.¹ The aluminised deposit, therefore, cannot really be regarded as containing cadmium in appreciable quantities.

Yours faithfully,

SHEILA M. HOLGATE, L.I.M.,

Technical Assistant to Managing Director,
Metallisation, Ltd.

Dudley, Worcs.

December 13th, 1955.

The Editor, METALLURGIA.

Sir,

The comments made by Miss Holgate are mainly amplifications of points made in our paper. The paper is based upon B.I.S.R.A. Report MW/C/21/55 and it was, perhaps, unfortunate that in condensing the report for publication certain explanations were considered to be somewhat unnecessary and were eliminated.

We would like to quote, for example, our original statement in the report regarding sprayed aluminium-silicon coatings, referred to in Miss Holgate's fourth paragraph: "The sprayed Al/Si coatings were specially prepared in order to examine the possibility of improved appearance after low temperature heating, as discovered with hot-dipped coatings. They are not used commercially." The next paragraph in the report referred to the "life expectancy due to thickness" mentioned by Miss Holgate (par. 2). The value of a preliminary heat treatment of sprayed coatings is twice referred to in this paper, when discussing Figs. 2b and 3b, which meets the first point raised.

We are glad that the views held by Metallisation, Ltd., do not differ essentially from our own, and we appreciate the interest which they have shown in our work.

Yours faithfully,

MARTIN L. HUGHES,

The British Iron and Steel Research Association,
South Wales Laboratories.

Sketty Hall,

Swansea.

December 16th, 1955.

Electronic Heaters for Australasia

REDIFON electronic heating equipment has been ordered for the General Motors Holdens plants in Adelaide, Australia and Wellington, New Zealand. Two heating installations are involved, the larger of which is bound for the Woodville Plant, Adelaide. This comprises two 20 kW. IH.43 induction heaters—each with its own work station—and an interconnecting conveyor. The purpose of the equipment is to braze the four lower control arm bosses to the front cross members of cars under construction by the company. It will be the most powerful radio frequency brazing equipment of its type in Australia.

The second installation, destined for New Zealand, comprises a Redifon RH.16 dielectric generator and a large welding press. It will be used to emboss and weld complete car door trims, and is identical to the equipment used by the Vauxhall Company in Britain in the production of Wyvern and Velox cars.

¹ B.I.S. 2569; Part 2; 1955

Sheath-Working of Metal Powders*

A sheath-rolling technique developed for the production of wrought products from metal powders is claimed to have a number of advantages over normal powder metallurgy methods. The present article is mainly concerned with titanium, but reference is made to the application of the technique to other metal powders, and to the consolidation of larger particles, such as drillings, chips, etc.

MANY of the difficulties associated with the production of metal sheet by normal powder metallurgy methods are said to be overcome by hot-rolling the powder within a closed sheath. In respect of homogeneity and absence of porosity, superior results are claimed in comparison with processes using pressed and sintered compacts, and a more effective welding together of the metal particles is attributed to a complete break-up of oxide and other films on the particle surfaces.

Because of its great chemical activity, titanium is not easily melted and cast as are the majority of other metals. At elevated temperatures, and especially in the region of its melting point, it not only reacts with the atmosphere to form the oxide and nitride, but also reacts with known refractories, reducing them and taking up oxygen from them. The oxide of titanium formed thereby is quite soluble in the metal and makes it brittle, rendering the titanium unsuitable for structural uses and difficult to fabricate by normal processes. Titanium must therefore be handled by special methods.

The New Technique

The diffusion processes necessary for solid-state welding of metal particles can be accelerated by providing maximum contact of the particles with each other, disrupting any surface films that may exist, destroying existing organised grain structures, and increasing the mobility of the atoms by heating to a temperature above the recrystallisation range, but below the melting point. If all these conditions can be met simultaneously, bonding of the particles can be accomplished speedily and with a minimum of effort. To do this by the new technique, the powder is packed in a sealed, ductile, gas-tight container and heated to the appropriate temperature; the assembly is then hot-rolled. The container protects the powder from harmful gases, such as oxygen and nitrogen, both during the heating and at the working temperature. It also confines the particles so that they are brought into contact with each other and are plastically deformed, destroying the tendency to bridge around voids, and disrupting any surface films which may be present. This direct contact of particles and the disorganisation of previous grain structures by the plastic deformation, together with the mobility of the metal atoms afforded by the high temperature, allows rapid diffusion and bonding between particles. As a result, solid non-porous metal is produced without the need for long sintering operations at high vacuum or the restriction in size imposed by the limitations of pressing equipment.

The process is applicable to metals other than titanium and is not confined to powders, since chips, machine turnings, cathode pieces, and other metallic particles or fragments may be treated in a similar manner. The method may also be used for the preparation of alloys

from mixed metal powders, with considerable advantage over normal powder metallurgy methods. Furthermore, the process is adaptable to the consolidation of particles of any mixture of metals that can be plastically deformed, if the proper choice is made of container and temperature range of deformation. Because of the confining action of the container, it may also be applicable to metals not usually considered workable. For example, brittle metals, if worked in this manner, may also respond, because the container maintains the metal fragments in contact with each other and allows rewelding of fractures formed by the working.

Consolidation of Titanium Powder

For the initial test in the experiments reported here, the powder was packed into a 6-in. length of standard $\frac{1}{2}$ -in. iron pipe, the ends of which were closed with iron plugs welded in place. The pipe, which had been carefully cleaned of scale and grease to avoid contamination, and its contents were heated to 700° C. and then hot-rolled, thereby reducing it to one-third its original thickness in three passes through the rolls. After reheating for 30 minutes it was again hot-rolled in two passes, finishing as a flat about $\frac{1}{16}$ in. thick. The titanium was removed from the sheath by cutting away the ends and edges of the iron. It showed no evidence of alloying with or welding to the iron, and therefore separated quite easily: the strip measured $0.048 \times 1 \times 10$ in. It was dense, compact metal closely resembling titanium prepared by the usual method of pressing the powder, sintering and then rolling the finished compact into strip.

In another experiment some 12 lb. of powder was sealed in a 20-in. length of standard 5-in. pipe whose ends were weld-closed. This pipe was flattened by cold-forging to a thickness of 2 in. so that it could be rolled in the mill available. It was then heated to 900° C. and hot-rolled, with frequent reheating to maintain this temperature. The titanium sheet produced measured 7 ft. in length and 7 in. in width and was $\frac{1}{16}$ in. thick. The edges of the sheet were rather ragged because of the folding of the pipe walls during the rolling, but the rest of the sheet was entirely satisfactory.

It was therefore obvious that sheath-rolling saved considerable time, effort and expense. However, loose titanium powder has a volume three to four times that of the solid metal and the initial rolling steps are largely expended in bringing the powder particles into contact with each other. The particles themselves are not deformed until the assembly has been reduced to less than one-third its original thickness. In practical application, it would be desirable to pack the container with the maximum amount of metal possible, so that the greatest benefit could be obtained from each step in the deformation. This would also reduce the volume of residual gas in the container, and greatly decrease possible contamination of the titanium. These gases could of course be displaced by inert gases such as helium

* Based on U.S. Bureau of Mines paper PB109118 obtainable from D.S.I.R., Regent Street, London.

TABLE I.—COMPARISON OF PHYSICAL PROPERTIES OF GREEN SHEATH-ROLLED AND STANDARD TITANIUM SHEET.

	Ultimate Tensile Strength lb./sq. in.	% Yield Strength (0.2% offset) lb./sq. in.	Proportional Limit (0.01% offset) lb./sq. in.	Elongation % on 2 in.	Hardness Rockwell C
Green Compacts Sheath-Rolled at 800° C. . . .	97,600	75,000	58,000	15.1	81
Standard Compacts Sintered and Cold-Rolled, and Annealed at 800° C. . .	79,100	64,000	58,000	24.7	76

and argon, or could be removed by evacuating the box before sealing. It appears, however, that simple displacement by packing the powder into the box under pressure or by pressing the powder into compacts before insertion in the box gives a metal: residual-gas ratio that is quite satisfactory.

Physical Properties of Sheath-Rolled Titanium Sheet

To show that the properties of the metal produced by the sheath-rolling technique are essentially the same as those produced by normal rolling, a number of green blocks were prepared from dehydrogenated powder (which gives slightly better results than standard powder, especially when the standard powder contains high percentages of hydrogen) and fabricated into sheet for tensile testing. The blocks were pressed in the standard way at 50 tons/sq. in. and measured $\frac{1}{8} \times 6 \times 10$ in. They were sealed in iron containers and hot-rolled at 800° C., with a reduction of 20% per pass, reheating between passes. The compacts were rolled parallel to the 10 in. dimension, producing sheet $\frac{1}{16}$ in. thick, 6 in. wide and several feet in length. Standard $\frac{1}{8}$ in. wide tensile specimens were cut. The tensile properties and hardness of the material are given in Table I, along with the properties of titanium produced by normal powder metallurgy.

These data indicate that the titanium sheet produced by this method compares favourably with the standard product. It has a higher tensile and yield strength, about the same proportional limit, a lower elongation, and a slightly higher hardness.

For cold-rolled tests, green $\frac{1}{8} \times 6 \times 10$ -in. pressed compacts were sheath-rolled in iron containers at 800° C. to a thickness of 0.104 in. These were then stripped from the container and cold-rolled to 0.0625-in. thickness. The data in Table II show that the green sheath-rolled material compares favourably with the standard sheet in regard to physical properties. Again the tensile strength is somewhat higher, the yield strength slightly lower, and the proportional limit and elongation considerably lower, while the hardness is slightly higher.

Alloys of Titanium

Alloys of titanium with a number of other metals have also been prepared by sheath-rolling the mixed powders at appropriate temperatures. The ease with which these alloys can be prepared in this manner is in distinct contrast to the time-consuming operations typical of the normal powder-metallurgy procedure. While it is quite possible to form homogeneous alloys by sintering powder metal compacts at high temperatures, the particle size of the powder, porosity of the compact, and surface films on the individual particles all act to hinder the diffusion processes necessary for producing homogeneous alloys, and prolonged sintering times are therefore required.

Alloys of titanium and copper, prepared by cold-pressing and sintering the mixed powders, were heated as long as 200 hours at 900° C. in unsuccessful attempts to attain equilibrium. At best, the alloys resembled non-homogeneous, porous castings, and had little value for determining characteristic structures and properties.

Titanium-copper alloys prepared by sheath-rolling were free of voids and gave every indication of complete diffusion of copper and titanium. Plastic deformation of the powders by sheath-rolling at temperatures high enough to permit rapid diffusion forms solid non-porous alloys in which the diffusion processes are complete, or nearly so, in a very short time.

Along the same lines titanium-iron alloys produced in this way were dense, homogeneous, single-phase metals, in contrast to the porous non-homogeneous material prepared by sintering. Alloys of titanium with nickel, cobalt, chromium and silicon have also been prepared by this method with similar results, and many other titanium alloys can be similarly treated.

General Applications

Although this procedure was originally developed for processing titanium powder to a usable shape for subsequent fabrication, it has a wide range of application to practically all metal powders or fragments. A number of experiments were made to demonstrate the possibility of using the process with representative metal powders, including chromium, tantalum, tungsten, molybdenum, beryllium, cobalt, iron and nickel. Larger metallic fragments, such as zirconium scrap turnings and pieces of electrolytically deposited chromium, cobalt, and manganese, were also treated by the sheath rolling technique.

The nickel and iron powders alloyed to the sheath and could not readily be removed. This is to be expected, under the circumstances, since both the iron and the nickel weld rather easily. The manganese broke up into relatively small fragments because of the allotropic change that occurs on cooling. The other metals were readily removed after the edges of the sheath were machined away.

The sheath-rolling of chromium powder is typical of the processing treatment for the metal powders and fragments in this series. Chromium powder of very fine mesh size was tamped into a $\frac{1}{2}$ -in. diameter hole, $5\frac{1}{2}$ in. deep, in a 6-in. length of 1-in. square cold-rolled iron. Suitable connections were made so that the air could be evacuated and replaced with helium, after which the seal was completed by welding a plug. The assembly was heated for 1 hour at 2,000° F. (1,100° C.) and hot-rolled, with 20% reduction per pass and reheating between passes, to a total of 50% overall reduction. A piece of chromium metal about $\frac{3}{4} \times \frac{3}{16} \times 8$ in. was obtained when the sheath was cut away. The metal was well bonded and its consolidation quite striking. Un-

TABLE II.—COMPARISON OF PHYSICAL PROPERTIES OF GREEN SHEATH-ROLLED AND STANDARD TITANIUM SHEET WITH 40% COLD WORK.

	Ultimate Tensile Strength lb./sq. in.	Yield Strength (0.2% offset) lb./sq. in.	Proportional Limit (0.01% offset) lb./sq. in.	Elongation % on 2 in.	Hardness Rockwell C
Green Compacts Sheath-Rolled at 800° C. and Cold-Worked 40% . . .	129,400	111,500	75,600	2.6	94
Standard Compacts Sintered and Cold-Rolled 40% . .	122,500	113,500	84,400	7.5	91

doubtedly use could be made of this technique for compacting high-purity chromium prepared by electrolysis or other methods. Chromium powder is very difficult to handle by conventional powder-metallurgy methods because its oxide film is very resistant to metallic diffusion and this results in poor bonding.

Beryllium powder is somewhat similar to chromium powder in that the oxide films hinder diffusion and produce weak bonds between the particles. Sheath-rolling provides clean, dense, coherent metal. Oxide in the powder is present in the boundaries of the beryllium grains. Cobalt, nickel and iron powders likewise can be handled very satisfactorily by the sheath-working technique. On the other hand, manganese, after treatment in the same manner, was extremely brittle and could not be handled after the sheath was removed. This is due to the normal cold brittleness of manganese and to the phase changes that take place in pure manganese.

Chromium and cobalt in the form of cathode chips were given the same treatment and produced good, dense metal. The ease with which the cathode chips of chromium, cobalt, and manganese were consolidated into solid metal with little or no void space is extremely interesting, since in packing these metals into the sheath, no particular effort was made to pack them or press them so as to reduce the void spaces in between the particles.

The metal used for the container and the operating temperature for the sheath-rolling are individually selected for each metal, and depend on such factors as the recrystallisation temperature of the metal being consolidated, and the ratio of the ductilities of container and

metal at the rolling temperature. In these experiments, iron was used as the sheath material; but other metals, such as aluminium, high-alloy steels, Monel, or molybdenum, would have specific applications. For satisfactory performance the sheath must be capable of being worked above the recrystallisation temperature of the metal being consolidated, and should not weld to the metal under the conditions used. This latter requirement is not too serious, since the sheath can be removed by a variety of methods; and, if necessary, contaminated surfaces of the consolidated metal may be machined off if alloying action does take place. It is believed that the reason the consolidated metal can be removed from the sheath so easily is either that the metal does not readily alloy with the sheath or that such alloying as does occur results in the formation of a thin brittle layer. This layer, being easily fractured, permits ready separation of the sheath and metal.

Molybdenum, tungsten, and tantalum, because of their high recrystallisation temperatures, should be sheath-rolled in containers capable of withstanding exposure to these high temperatures; however, preliminary tests were conducted in iron sheaths rolled at 2,000° F. (1,100° C.). The tantalum powder was very well bonded by this treatment, but molybdenum and tungsten were only partially bonded. Nevertheless, the results demonstrate that the method is applicable to these metals, and that the use of a more suitable sheath material, which would permit working them above their recrystallisation temperatures, would undoubtedly produce dense, well-bonded metal.

Plant Engineers' Refresher Course

THE Education Committee of Incorporated Plant Engineers announce that their comprehensive Refresher Course for Works and Plant Engineers in London and the Home Counties, which commenced at The Royal Empire Society in November, has surpassed the enrolment records set up by their previous courses in other parts of Britain. 550 engineers have been entered for it, and some hundreds of further applications have had to be declined because of accommodation limitations.

The Committee have now organised a shortened version of the London Refresher Course for the benefit of senior works and plant engineers in Hampshire and the adjacent counties. Sponsored by Sir Henry Tizard, G.C.B., D.Sc., F.R.S. (Pro-Chancellor of the University of Southampton), it will consist of 12 weekly lectures from the London Course syllabus given by the same lecturers, and will be held at Southampton University on Tuesday evenings, commencing on January 17th.

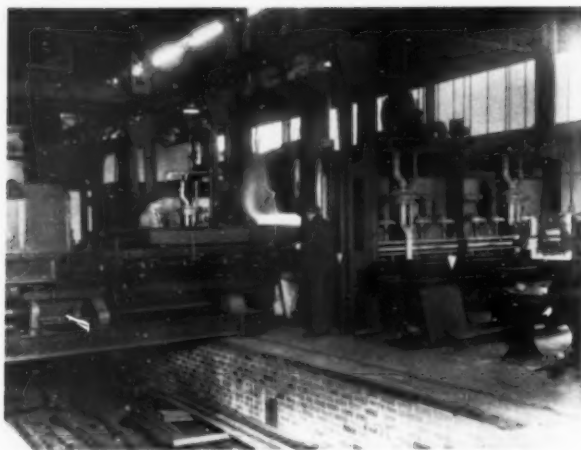
Designed, like the London Course, to encourage the most effective use of existing knowledge, and to promote the application of up-to-date techniques in works engineering practice over a broad field, its purpose is to help works and plant engineers make the fullest possible contribution to increasing productivity. The subjects include: planned maintenance; lubrication; combustion and steam raising; oil firing; space heating; steam utilisation; electrical switchgear and factory distribution systems; automatic process control; materials handling; compressed air plant; and the plant engineer and management.

The fee for the course is two guineas, and copies of the syllabus and full particulars may be obtained from the Secretary to the Refresher Course, The University, Southampton (tel.: Southampton 54071).

N.R.C.-Degussa Agreement

NATIONAL RESEARCH CORPORATION, Cambridge, Massachusetts, has signed an agreement with Deutsche Gold- und Silber-Scheideanstalt, A.G., Frankfurt-am-Main, Germany, ordinarily referred to as Degussa, for an exchange of information relating to high vacuum furnaces. For a period of 15 years National Research Corporation has been the leading producer of industrial vacuum furnaces in the United States and Vacuum Metals Corporation, owned jointly with Crucible Steel Company of America, is the country's first and largest producer of vacuum melted metals and alloys. N.R.C. has designed and built many of the vacuum melting furnaces for the United States atomic energy programme, and for a number of industrial and research installations in the United States.

Degussa, one of Germany's principal inorganic chemical and metallurgical companies, also has substantial equipment manufacturing operations. The company has specialised in the production of sintering furnaces for hard metals and carbides, and in vacuum and controlled-atmosphere heat-treating furnaces. Through the new agreement, this know-how will be made available to N.R.C. for the production of furnaces in the United States.



A charge being inserted into the furnace.

AN essential feature of the production of tool steel bars is the annealing operation which removes any undesirable structural characteristics and internal stresses resulting from casting and working. Cored dendritic structures present after casting show segregation of the more highly alloyed material, and although hot working largely corrects this, a final heat treatment is necessary to readjust the crystal form and soften the material. It is essential in the case of most tool steels to produce an annealed structure suitable for hardening.

The structure most suitable for subsequent heat treatment is that of uniformly spheroidised cementite in a matrix of ferrite. Providing the steel has been hot worked within the correct temperature range, thus ensuring a fine pearlite structure with no excessive grain boundary cementite, a spheroidised structure can be obtained by heating to just below the A_{c1} temperature and holding for sufficient time for the original pearlite lamellae to form carbide spheroids. The steel is then slowly cooled in the furnace.

Although annealing by the above method is satisfactory for steel hot worked under optimum conditions, it is generally safer to give a full anneal. This involves heating to a temperature above the A_{c1} point without attempting to dissolve all the carbide, but for a time sufficient to ensure that grain boundary cementite is sufficiently broken down to facilitate spheroidisation during the slow cooling through lower temperatures.

Isothermal Annealing

Fairly long time cycles are necessary to obtain satisfactory structures by this method, but this difficulty can be overcome by the adoption of isothermal annealing. With the help of the appropriate time-temperature-transformation diagrams, good annealed characteristics can be obtained by heating to a pre-determined temperature above the A_{c1} point, holding to allow the necessary structural changes to take place, and cooling quickly to the appropriate temperature below the critical range, this temperature being maintained for a sufficient period to spheroidise the structure. The steel may then be withdrawn from the furnace and allowed to cool. This method offers some saving in both time and fuel, but close control of furnace temperatures is essential if poor annealed structures are to be avoided.

Tool Steel Annealing

New Facilities for Arthur Balfour & Co., Ltd.

Some ten years ago, Arthur Balfour & Co., Ltd., commenced a programme of laboratory and semi-works isothermal annealing trials, the encouraging results of which led to trials using production quantities of steel and production equipment. As a consequence of this work, the company has, for several years, adopted isothermal annealing for a substantial proportion of its semi-finished and finished bar tool steels. For some time limitations of annealing equipment prevented full-scale application of the method, but with the inauguration of the new heat treatment plant at the Broughton Lane Works this goal has now been achieved. Isothermal cycles have been determined for the whole range of plain carbon, alloy and high speed tool steels made by the company.

New steels and treatments, and the need for a higher standard of annealing, have greatly influenced furnace design, firing methods, handling methods, and temperature measurement and control. There has been a complete reversal from the high thermal storage capacity furnace, so essential to the original "slow cool" annealing process, to the hot face insulated low thermal storage furnace necessary for the rapid temperature changes of the isothermal annealing cycle. A feature of the isothermal annealing process is the fact that the charge is in the furnace for a pre-planned period of time, sufficient to complete the metallurgical changes, and then withdrawn whilst at a temperature in the range 600° – 780° C. and a fresh charge placed in the furnace. In the past, this hot discharging and charging of furnaces has presented something of a handling problem with the relatively crude equipment available at the old furnaces. This has been solved by the installation of an electrically operated charging machine.

Three Furnaces

The new heat treatment plant consists of three Gibbons batch type furnaces each having a heating chamber 5 ft. wide \times 2 ft. high \times 16 ft. long, one Gibbons van Marle electric charging machine and two fabricated steel loading tables.

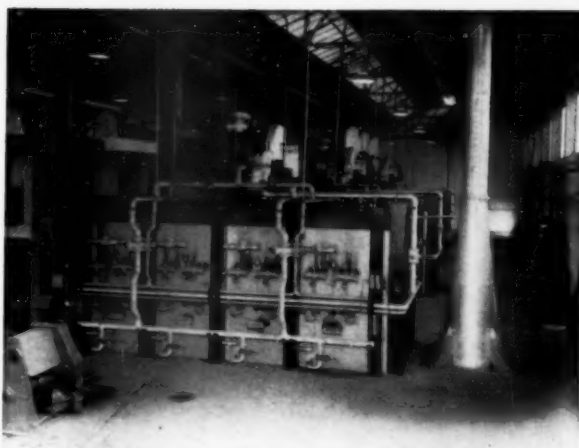
The furnaces are fired by town's gas on the Gibbons-Webb roof combustion system, augmented by special long flame burners firing into transverse slots below the hearth level. This dual firing arrangement ensures

uniform temperature distribution for all types and dispositions of load, and also enables varied rates of heating and low temperature treatment to be carried out satisfactorily.

The roof combustion system embodies an arch perforated with regularly spaced holes of uniform size, through which preheated combustion air flows in the form of small jets into the fuel gas below. The gas is introduced through regularly spaced ports along each side of the furnace, immediately below the springing line of the roof arch, and the resultant combustion produces a blanket of flame of great uniformity across the width and along the length of the furnace chamber. The combustion gases, after enveloping and heating the load, are evacuated through regulatable ports in the furnace hearth into two recuperator chambers immediately below, and after passing over the recuperator tubes they finally flow into the chimney.

Each burner section has its own metallic recuperator, in the form of aluminised hair-pin shaped tubes, for preheating the combustion air. Each tube is fitted with a control valve on the cold air inlet side. Air is supplied under pressure from an electrically driven fan: after passing through the recuperator tubes it flows through insulated pipes contained in the double channel furnace buckstays, and then enters a hot air reservoir built in brickwork above the perforated roof, from which it descends through the jets previously mentioned into the heating chamber.

Each furnace is divided into two temperature control zones for the roof combustion system, and each zone is governed by Kent variable-speed floating and proportional controllers, which operate automatic combined air/gas valves. This type of equipment ensures close temperature control over the wide range of fuel supply associated with long heat treatment cycles, where the load is raised to temperature and then held at that temperature or allowed to cool slowly over a period of several hours. Accurate temperature control is obtained at all heating rates, and the furnace operator is relieved of the responsibility for resetting valves and dampers when changing to new control temperatures. The automatic air/gas control valves are designed to give a constant air: fuel ratio over the whole range of valve opening, and it is, of course, possible to vary this air:



End view of the new furnace installation.

fuel ratio to give oxidising or reducing conditions in the furnace atmosphere.

The chimney damper is automatically controlled by means of an Electroflo regulator, which varies the damper opening to suit the fuel input, thus maintaining a constant positive pressure in the furnace chamber. In order to obtain optimum thermal efficiency, the design incorporates the extensive use of hot-face and normal insulating bricks. The side walls of the heating chamber are built in hot-face materials.

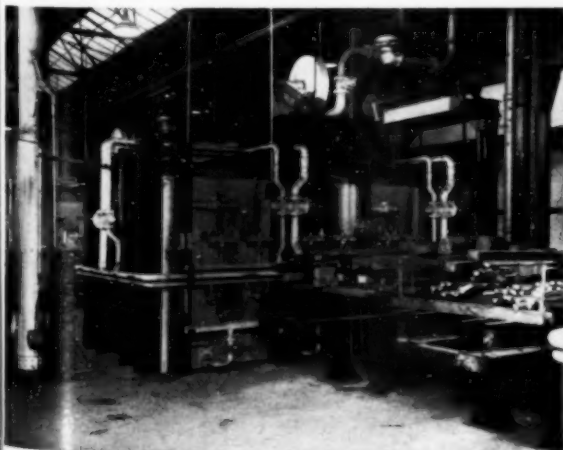
Charging Machine

The hearth is furnished with three longitudinal slots. The centre one is used as a collecting duct for the hot gases prior to their leaving the chamber, and the two outer ones, which are fitted with flat heat resisting steel rails, are for receiving the arms of the charging machine which handles the load into and out of the furnace.

The charging machine has two arms which carry the load into the furnace in one movement. The arms are of a special design, formed of two horizontal members—one above the other. The lower arms each consist of two mild steel flat bars between which is a series of cast iron rollers for taking the weight of the load when on the machine chassis, and also in the furnace. The upper arms are also made of mild steel flat bars which can be raised or lowered by means of rollers running upon cast iron inclined planes also built into the lower arms.

During the charging operation, the arms are expanded with the load resting on them and then advance into the slots in the furnace hearth. The rollers in the lower members of the arms run on the rails at the bottom of the slots so that all cantilever action on the machine chassis is avoided. When the arms are fully extended with the load, the upper members of each arm are lowered until the load rests upon the furnace hearth, the arms then contract still further so that they are free to be withdrawn from underneath the load. The total charging time is approximately 1½ mins. between the opening and closing of the furnace door.

When a load is being discharged, the arms are extended into the furnace in their lowered position and when fully extended under the load they are expanded so that they lift it free from the furnace hearth: it is then withdrawn and the door closed. The machine can



Assembly of material on the loading tables.

then travel along in front of the furnace and deposit the load on to one of the discharge tables.

The machine is capable of carrying a maximum load of 10 tons and has a travelling speed along the shop rails of about 100 ft./min. It is fitted with three motors, one for lifting, one for traversing the arms into and out of the furnace, and the third for travelling along the shop floor. Electrical interlocks are provided so that it is impossible for the machine to travel in either direction unless the arms are fully withdrawn from the furnace slots.

Control of Product

In deciding upon the equipment and layout of the department, means for checking and control of the quality of annealing have not been overlooked. For this purpose there have been installed an Avery power-operated Brinell hardness testing machine, a Firth 120 kg. Hardometer, and a bench metallurgical microscope, together with the means for preparing micro-sections for on-the-spot microstructural examination. Brinell hardness limits have been drawn up for all the Balfour tool steels, together with standards for microstructural condition.

Control covers the checking for Brinell hardness of every individual charge, which must conform to the

strict limits imposed. In the case of steels which experience has shown to be very susceptible to the effects of previous rolling and forging treatments, the control is extended to the hardness testing of each individual bar. A further feature of the control is the micro-structural examination and surface decarburisation testing of a representative sample of the daily production.

Part of Larger Scheme

The new heat treatment plant is part of a much wider scheme of over-all modernisation, part of which has been completed, including the new steel warehouse. Previously, bar annealing had been carried out simultaneously in two different works, two furnaces being situated at the Wicker, and one at Broughton Lane, two and a half miles away. All the furnaces were exactly similar, being fired by pulverised coal, fed from a 10-ton hopper, blown and mixed with air to be finally ignited in a combustion arch below the hearth level. The new installation is sited partly in the old annealing shop and partly in a new bay. The old bay has been adapted to house the charging machine and the new bay is occupied by the gas fired furnaces. Space is available alongside the existing furnaces for three further furnaces of a similar type for future expansion.

In the New Year Honours List

KNIGHTHOOD

CHARLES CONNELL, Chairman, Charles Connell and Co., Ltd.
HENRY FRANK HARDING JONES, M.B.E., Deputy Chairman, Gas Council.

WILLIAM LYONS, Chairman and Managing Director, Jaguar Cars, Ltd.

PROFESSOR SOLLY ZUCKERMAN, C.B., Deputy Chairman, Advisory Council on Scientific Policy.

K.C.B.

SIR FREDERICK BRUNDRETT, K.B.E., C.B., Chairman, Defence Research Policy Committee and Scientific Adviser to the Minister of Defence.

C.B.

W. CAWOOD, C.B.E., Principal Director of Scientific Research (Air), Ministry of Supply.

W.C.M. COUCH, C.B.E., Deputy Director of Electrical Engineering, Admiralty.

K.G.B.E.

SIR JOHN MORISON, Chairman, Iron and Steel Holding and Realisation Agency since 1953.

D.B.E.

KATHLEEN, MRS. LONSDALE, Professor of Chemistry and Head of the Department of Crystallography, University College, University of London.

K.B.E.

SIR CLAUDE DIXON GIBB, C.B.E., Chairman, C. A. Parsons and Co., Ltd.

C.B.E.

H. V. DISNEY, Chief Engineer, Industrial Group Headquarters, Risley, United Kingdom Atomic Energy Authority.

R. GRAHAM, Director of Aircraft Research and Development, Ministry of Supply.

H. F. HODGSON, Managing Director, Joseph Sankey and Sons, Ltd.

P. E. R. JEFFRIES, Chief Surveyor, Admiralty.

R. S. STAFFORD, Technical Director, Handley Page, Ltd.

G. STEEL, J.P., General Managing Director, The United Steel Companies, Ltd.

O.B.E.

F. J. COWLIN, Chief Engineer, Steam Turbine Division, English Electric Co., Ltd.

D. G. DUFF, Lubricating Oil Adviser, Ministry of Fuel and Power.

F. GREENWELL, Secretary, British Coking Industry Association.

F. HEAP, Chairman, Association of Steel Drum Manufacturers.

W. J. HUGGETT, Manager, Marine Department (Carrier Equipment), General Electric Co., Ltd., Fraser and Chalmers Engineering Works.

H. PARISH, Chief Engineer, Henry Wiggin and Co., Ltd.

F. H. PERKINS, Education Officer, Imperial Chemical Industries, Ltd.

G. A. V. TYSON, Chief Test Pilot, Saunders-Roe, Ltd.

M.B.E.

K. H. BEALE, Dry Dock Manager, Smith's Dock Co., Ltd.

F. BINGLEY, General Manager, Dallow Lambert and Co., Ltd.

A. BOWEN, Mechanical Engineer, British Thomson-Houston Co., Ltd.

R. C. BUTTERS, Chief Machine Progress Superintendent, English Electric Co., Ltd.

F. A. CROUCH, Inspector, Aeronautical Inspection Directorate, Ministry of Supply.

J. S. CURPHEY, Steel Plant Manager, Dorman Long (Steel), Ltd.

G. E. DREWETT, Divisional Superintendent, Westinghouse Brake and Signal Co., Ltd., Chippenham.

E. T. GRATTIDGE, Chief Engineer J. M. Henderson & Co., Ltd.

J. HAIGH, Draughtsman, Whipp and Broune Ltd.

R. HAWORTH, Chief Draughtsman, Santon Ltd.

A. IBBOTSON, Chief Draughtsman, Plant Department, Metropolitan-Vickers Electrical Co., Ltd.

F. N. JUDSON, Industrial General Sales Manager, Mobil Oil Co., Ltd.

W. S. MARTIN, Chief Inspector, Brown Brothers (Aircraft), Ltd.

D. C. ROGERS, Section Head, Standard Telephones and Cables, Ltd., Ilminster.

W. R. ROSE, Chief Mechanical Designer, General Electric Co., Ltd., Telephone Works, Coventry.

C. E. WHITE, Assistant General Manager (Production), Brooke Marine, Ltd.

H. C. WILLIAMS, lately Fitting Shops Manager, The Bristol Aeroplane Co., Ltd.

J. G. P. ZIEROLD, Technical Manager, Briggs Motor Bodies, Ltd.

B.E.M.

N. BAXTER, Electrical Tester, Metropolitan-Vickers Electrical Co., Ltd.

H. COLE, Toolroom Foreman, Joseph Lucas (Batteries), Ltd.

H. J. DIXON, Foreman, Civil Reserve Oil Installation (Stourport), Regent Oil Co., Ltd.

T. KNOX, Chargehand, R. & H. Green and Silley Weir Ltd.

J. LEWIS, Assistant Mill Foreman, Gorse Galvanising Co., Ltd.

A. McGOWAN, Foreman of Plumbers, Harland and Wolff, Ltd., Southampton.

J. W. McIVOR, Electrician, Imperial Chemical Industries, Ltd., Billingham.

C. MOULT, Senior Engine Erector, Crossley Premier Engines, Ltd.

R. STRACEY, Ship Plater, Mercantile Dry Dock Co., Ltd. (Jarrow).

A. A. F. TATMAN, Chargehand, Enfield Cables, Ltd.

MISS MAUD UNWIN, Fitter, Dewrance and Co., Ltd.

E. YATES, Foreman Electrician, Beyer, Peacock and Co., Ltd.

NEWS AND ANNOUNCEMENTS

Summer School on Water Treatment

THE third Summer School on Corrosion, which has been organised in conjunction with the Corrosion Group of the Society of Chemical Industry, will be held at Battersea Polytechnic from July 17th to 20th, 1956. The topic will be water treatment, and should be of interest to chemists, engineers and others who are concerned with this subject.

The syllabus will deal with the following aspects: types of water and their properties; electrochemical principles of corrosion; inhibition of corrosion by waters; materials of construction; precipitation methods of water softening; ion exchange methods of water treatment; steam boiler feed water treatment; circulating water treatment; and examples of industrial problems. In addition to the lectures there will be a demonstration of methods of water treatment and control analysis. A visit to a power station and water works has also been arranged.

The inclusive fee for the Summer School is £4 4s. Accommodation is available at the Polytechnic Hostel during the Summer School at an inclusive fee of £5 5s. Particulars can be obtained from the Secretary, (Corrosion S.S.), Battersea Polytechnic, London, S.W.11.

Symposium on Extraction Metallurgy of the Less Common Metals

As previously announced, a Symposium on the Extraction Metallurgy of some of the Less Common Metals is being organised by the Institution of Mining and Metallurgy, and will be held in the Lecture Hall of the Royal Society of Arts, 6, John Adam Street, Adelphi, London, W.C.2, on Thursday and Friday, 22nd and 23rd March, 1956.

A provisional list of papers to be presented has been issued, and includes the following:—

Some General Chemical Principles in Extraction of Metals from Low-Grade Ores, by A. J. E. WELCH.

The Thermochemistry of Reduction Processes, by J. S. BROADLEY et al.

Purification by Solvent Extraction, by J. M. FLETCHER.

Metallurgical Developments in the Recovery of Some of the Less Common Metals in Canada, by L. E. DJINGHEUZIAN.

An Oxide-Chloride Conversion Process for the Extraction of Certain Metals, by A. R. GIBSON.

Extraction of Less Common Metals from Smelter and Refinery Intermediates at La Oroya, Peru (Selenium, Tellurium and Thallium), by W. E. KOEPEL and A. E. SCHELLINGER.

Chlorination of Some Complex Ores—Wolframite, Vanadinite and Chromite, by E. A. POKORNY.

The Production of High-Purity Vanadium Metal, by E. FOLEY, MRS. M. WARD and A. L. HOCK.

Processes for the Extraction of Vanadium, by C. TYZACK and A. F. ADAMSON.

Flotation of Vanadium Ore from the Abenab West Mine of the South West Africa Company, by M. F. FLEMING.

Factors Influencing the Magnesium Reduction of UF_4 , by J. HARPER, W. G. O'DRISCOLL and A. E. WILLIAMS.

Chemical and Physical Concentration of Uranium Ores, by S. W. F. PATCHING.

The Recovery of Uranium from Leach Liquors by Ion Exchange, by T. V. ARDEN.

Consideration of Methods for the Extraction of Thorium, by A. B. MCINTOSH, A. AUDSLEY and R. LIND.

The Preparation of Beryllium Metal by Thermal Reduction of the Fluoride, by L. J. DERHAM and D. A. TEMPLE.

Purification of Metals by Intermediate Formation of their Stable Halide Vapours, with Application to Beryllium and Titanium, by P. GROSS and D. L. LEVI.

Beryllium Production at Milford Haven Plant, by P. S. BRYANT.

A Review of the Methods for the Extraction of Pure Niobium, by A. B. MCINTOSH, G. K. DICKSON and J. A. DUKES.

Distillation of Volatile Chlorides as a Means of Obtaining Pure Niobium, by J. S. BROADLEY and B. R. STEELE.

The Extraction of Pure Niobium by a Chlorination Process, by A. B. MCINTOSH, J. S. BROADLEY and A. E. WILLIAMS.

The Manufacture of Hafnium-free Zirconium, by J. M. HUTCHESON and F. HUDSWELL.

Some Investigations into the Extraction of Titanium by Fused Salt Electrolysis, by F. L. BETT, B. S. HICKMAN, G. M. WILLIS and H. K. WORTER.

Attendance at the meeting is open to all interested persons and is not restricted to members of the Institution. A charge of £1 10s. will be made to members of the Institution and of £3 to non-members. This will entitle them, without further charge, to a set of the advance papers and one copy of the Proceedings of the Symposium. All communications concerning the Symposium should be addressed to the Secretary, Institution of Mining and Metallurgy, 44, Portland Place, London, W.1.

Further Suspension of Iron and Steel Import Duties

UNDER the Import Duties (Exemptions) (No. 7) Order 1955, the import duties on a wide range of iron and steel products are suspended until March 18th, 1956, while those on certain cold-rolled sheet are suspended until September 18th, 1956.

After consultation with the Iron and Steel Board about the supply position, Her Majesty's Government have decided to make a new Order which prolongs these temporary suspensions of import duty for a further six months, i.e., until September 18th, 1956 (with an amendment to the description of plates and sheets to cover those imported in the form known as circles) and March 18th, 1957, respectively. The new Order does not extend beyond March 18th, 1956, the existing suspension of import duty on blast furnace ferro-manganese. The Government have undertakings from the producers and the main consumers of tinplate that all available home-produced tinplate including the full output from the hand mills will be taken up while the duty on tinplate and tinned sheets remains suspended.

This new Order, the Import Duties (Exemptions) (No. 11) Order, 1955 (S.I. 1982), came into operation on January 9th, 1956. Copies of the Order may be obtained from Her Majesty's Stationery Office or from any bookseller, price 3d. (by post 4½d.).

Birlec Equipment at Kirkby

BRIEF details of the Birlec equipment installed at the Kirkby Works of Imperial Chemical Industries, Ltd., have recently been released. It comprises three furnaces, one for billet heating and the other two for annealing the tubes produced from the billets.

The billet furnace, constructed to accept copper billets 3 in. to 6 in. in diameter, 72 in. long, is gas fired and heats them to 850°C. for piercing, maintaining this

temperature to within $\pm 5^{\circ}\text{C}$. The furnace, which is capable of handling $8\frac{1}{2}$ tons per hour, is of gas-tight construction and is fired by open-type burners. Automatic charging from the billet magazine is effected by means of a screw conveyor system, in which the billet is supported by raised guides so that the screw merely propels the billets forward and does not bear their direct weight. The outstanding feature is the special control of combustion, ensuring the production of completely scale-free billets. This Birlec development has since been applied to a number of other copper billet heating furnaces.

In addition to the double-screw conveyor furnace, two electrically heated roller hearth conveyor furnaces have been installed. The first, for intermediate clean annealing of straight copper tubing up to $2\frac{1}{2}$ in. diameter, normally handles lengths up to 75 ft. Operating at 550°C ., the furnace is rated to produce 3 tons per hour, and annealing is carried out in an atmosphere produced from town's gas. The second, for bright annealing copper tubing at 550°C ., handles both straight lengths up to 60 ft. and tubing in 5 ft. diameter coils, the atmosphere also being derived from town's gas.

N.P.L. Acting Director

THE resignation of Sir Edward C. Bullard, F.R.S., from the Directorship of the National Physical Laboratory, took effect on December 31st, 1955. The appointment of a successor to Sir Edward Bullard will be announced in due course. In the meantime, and pending the taking up of office by a new Director, the Lord President of the Council has appointed Dr. R. L. Smith-Rose, C.B.E., Director of Radio Research in the Department of Scientific and Industrial Research, to be Acting Director, with effect from January 1st, 1956.

Institute of Welding Awards

THE Council of The Institute of Welding has awarded the Sir William J. Larke Medal for 1955 to Mr. J. G. YOUNG for his paper "Construction of the All-Welded Twin-Screw Auxiliary Motor Yacht *Morag Mhor*." This medal is awarded annually to the author whose paper is judged to be the best previously unpublished contribution presented to the Institute or its Branches during the past session. Mr. Young's paper appeared in the January 1955 issue of the *British Welding Journal*.

The winner of the 1955 C. W. Hill Prize Competition is Mr. A. J. A. COOKSEY, Associate of the South London Branch. The Council has also approved the award of a supplementary prize to Mr. P. J. LANCASTER, Associate, North London Branch, whose entry was specially commended.

S.C.I. 75th Annual Meeting

"ACHIEVEMENTS of Industrial Chemistry" is to be the theme of the 75th Annual Meeting of the Society of Chemical Industry in London this year. The nature of the lectures will be such as to enable speakers to review the major advances brought about by the work of industrial chemists in the last 25 years, and to look forward over the next 25 years to the centenary of the Society. After a general introduction, there will be two parallel series of lectures, each of four. One series will deal with the products of industrial chemistry, the new processes which have been evolved and perfected, and

the advances in fundamental science which made them possible. The other series will survey the tools of industrial chemistry to-day, and cover such subjects as modern manufacturing techniques and the use of metals and non-metals in plant construction.

H.R.H. The Duke of Edinburgh Visits Electroflo

ON his recent visit to the Maryport Factory of Electroflo Meters Co. Ltd., H.R.H. The Duke of Edinburgh expressed his interest in the great and ever-widening part that instrumentation and automatic control is playing in manufacturing and processing industries.

The Duke was shown the manufacture of industrial instruments right from their "raw material" stage, through the various checking processes, to assembly, and final testing. He was impressed by the clean looks of instrument and control panels, and by the neat and orderly wiring and piping arrangements inside. His Royal Highness was conducted round the factory by the Chairman and Joint Managing Director, Mr. B. Dunglinson, and Mr. J. A. Hackett, Works Manager. The Duke chatted with Mr. W. P. (Paddy) Kelly, who was blinded in Holland during the Second World War. Previously a steeplejack, and trained by St. Dunstan's, Kelly is now able to operate a press and other plant with great efficiency. Another worker with whom the Duke talked was Mr. J. Dawson, who was invalided out of a coal mine owing to long and serious illnesses, but is now happy and confident in his work in charge of an assembly section. During the visit, the Duke was presented by Mr. Dunglinson with a model traction engine for Prince Charles, made by Mr. John Sharp, a member of the Cumberland Guild of Model Engineers and Craftsmen. Many members of the Guild are employees of Electroflo, and are allowed the facilities of machines at the Electroflo factory for model-making in their spare time.

The factory, situated in what was one of the worst-hit areas of industrial depression, employs hundreds of workers, many of whom endured long spells of unemployment, and who find new hope and enthusiasm in this thriving industry.

Primary Aluminium Price

ALUMINIUM UNION, LTD., distributors of Canadian primary aluminium ingot in this country, announce that effective January 1st, 1956, the price of primary aluminium 1-20K ingot of 99.5% minimum purity delivered to industrial users in the United Kingdom is £179 per long ton. The premiums applicable for the metal in higher purities and in different forms remain unchanged.

Aluminium Watches Presented

TWELVE employees of Northern Aluminium Company's Birmingham and Banbury Works were on December 7th and 9th presented with watches to mark their 25 years' service with the Company. The presentations were made by the Managing Director, Mr. FRASER W. BRUCE, at four separate functions held at the respective Works and at Chadwick Manor Hotel, Knowle.

Gold wrist watches were presented to Miss E. BUSSWELL, who had been telephone operator at the Birmingham Works for 25 years, Miss I. K. HOWARD, Treasury Department, Banbury Works, and Miss A. SWITZER, Metal Purchasing Department, Banbury Works. Alu-

minium pocket watches, specially made for the Company by a famous Swiss firm and weighing only about half an ounce each, were presented to (Birmingham Works): Mr. B. ASHTON, Coremaker; Mr. R. H. FELLOWS, Development Superintendent; Mr. C. HAMPTON, Fetter; Mr. W. T. WRIGHT, Moulder; and (Banbury Works): Mr. S. C. BEENY, Chief Buyer; Mr. I. L. GOODALL, Chief Engineer; Mr. H. O. A. HOLT, Chief Draughtsman; Mr. F. J. MAYFIELD, Costs Department, and Mr. W. J. NORMAN, Assistant Buyer.

The guests at each presentation included Mr. C. P. PATON and Mr. B. N. H. THORNELY (Directors), the Works Managers and Heads of Departments. The presentation at Chadwick Manor Hotel, Knowle, was noteworthy in bringing together 30 employees of the Birmingham Works who had received aluminium watches in previous years, including four brothers JOHN, IVOR, WILLIAM and RICHARD DAVIES who have served the Company for a total of 129 years, and two other brothers EDWARD and THOMAS PARKES.

Industrial Statistics Course

ORGANISED by the Extra-Mural Department of the University of Manchester, a Course of 10 Lectures on "Statistical Methods with Special Reference to Industrial Applications" will be held in the Dover Street Building of the University commencing on January 16th, and will continue on successive Monday evenings at 7 p.m. Tickets for the Course can be obtained on payment of a fee of 10s. from the Director of Extra-Mural Studies, The University, Manchester, 13.

Welding and Productivity

THE Nottingham Meeting on "Increasing Production by Recent Developments in Welding and Design Techniques" will be held on Tuesday and Wednesday, February 7th and 8th, at the Nottingham Mechanics' Institution, Trinity Square, Nottingham. This is the sixth of a series of two-day meetings arranged by the British Welding Research Association at various centres throughout the country.

G.E.C. Preston Depot

THE General Electric Co., Ltd., has opened a new depot at Magnet House, Derby Street, Preston. The new depot, under the management of Mr. R. G. Galloway, will be able to give better delivery services in the North Lancashire area than has hitherto been possible. The trade will also benefit from increased stocking and counter facilities. The telephone number of the Preston Depot is Preston 57871/2.

Dowson and Mason, Ltd.

BECAUSE of the extension of the Company's activities in recent years, the name of The Dowson and Mason Gas Plant Co., Ltd., of Levenshulme, Manchester, 19, has been changed to Dowson and Mason, Ltd.

Winston Electronics, Ltd.

THE telegraphic and cable addresses of Winston Electronics, Ltd., Shepperton, Middlesex, have been changed from "Control, Shepperton," to "Winston, Shepperton."

Personal News

DR. T. P. HUGHES has been appointed Director of the Tube Investments Research Laboratories at Hinxton Hall, Cambridge. Dr. Hughes was Head of the Chemistry Department and subsequently Chief Superintendent of the Rocket Propulsion Department of the Royal Aircraft Establishment before joining Tube Investments, Ltd.

THE DIRECTORS of The Effingham Steel Works, Ltd., Sheffield, have announced the appointment of their General Manager, Mr. J. H. ALLAN, as a Local Director of the Company, and of Mr. HEDLEY LLOYD as a Special Director of the Company with reference to Export Duties.

MR. W. D. PUGH has relinquished the office of Managing Director of The Darlington Forge, Ltd., and has been appointed Deputy Chairman. Mr. W. S. SCOTT is appointed Managing Director and Dr. C. J. DADSWELL a Director.

MR. P. F. HANCOCK, Research Manager, Mr. A. E. PICKLES, Manager of the Induction Heating Division, and Mr. J. F. ROSS, Works Manager, have been appointed Directors of Birlec, Ltd.

MR. R. W. EVANS, formerly Melting Shops' Superintendent, has been appointed Assistant General Manager (Operations) of The Steel Company of Wales, Ltd. Mr. I. S. SCOTT-MAXWELL, who until now has held the position of Chief Engineer, has been appointed Assistant General Manager (Engineering and Development).

MR. W. E. A. REDFEARN has been appointed Assistant Managing Director of English Steel Forge and Engineering Corporation, Ltd.

MR. P. J. C. BOVILL, J.P., Assistant Managing Director of Newton Chambers and Co., Ltd., Sheffield, has accepted an invitation to join the Board of The Wellman Smith Owen Engineering Corporation, Ltd. This will strengthen the close association which has existed for a number of years between the two companies, of both of which Mr. P. G. ROBERTS, M.P., is Chairman.

MR. C. A. HAGLUND has retired from the position of Managing Director of the Electric Furnace Products Co., Ltd., of Sauda, Norway, and is succeeded by Mr. H. BLEGEN.

Obituary

WE regret to record the sudden death at a Reading nursing home on Saturday, December 17th, of Mr. A. B. OWEN, Extrusion Manager and Assistant Production Manager of the Banbury Works of Northern Aluminium Co., Ltd. Mr. Owen, who was 41, was a mechanical engineer by profession, was educated at Christ's Hospital and University College, London, where he obtained his B.Sc. (Eng.) degree. He joined Northern Aluminium Company in October, 1939, and from October, 1942, to April, 1943, was Extrusion Manager at Adderbury Works. After a period of two years as assistant in the extrusion office at Banbury he was appointed to the General Engineering Department, which was responsible for the design and erection of the continuous strip mill at Rogerstone Works. In January, 1951, he returned to Banbury as Extrusion Manager, an appointment he later combined with that of Assistant Production Manager.

RECENT DEVELOPMENTS

MATERIALS : PROCESSES : EQUIPMENT

Thermostatic Bi-metal

AN announcement by British Driver-Harris Co., Ltd., will be of particular interest to users of thermostatic bi-metal. This Company can now supply thermostatic bi-metal for a wide range of industrial and domestic applications. A new Bi-metal Section has been established to deal with all aspects of research, production and marketing. This announcement comes after a lengthy period of research by the Company in collaboration with W. M. Chase Co. of America, during which time production and processing techniques have been under continuous investigation. Particular stress has been laid on quality control at every stage of production, and on rigorous testing of the finished material both in the works and in the laboratories. Thermostatic bi-metal is available in all the standard types, it can be supplied in sizes to meet individual requirements and extremely good delivery can be quoted.

Bi-metal Section, British Driver-Harris Co., Ltd., Manchester, 15.

Hydraulic Press Brake

THE Craig Donald Branch of the Scottish Machine Tool Corporation, Ltd., who have been making the mechanical type of press brake for many years, have recently introduced a 100-ton hydraulically operated unit. The length of the die space is 10 ft. 1 in., the width between the housings 10 ft. 6 ins., the stroke of the moving slide 9 in., and the depth of the gap 10 in. The brake is capable of bending to a right angle, when suitably tooled, a mild steel plate 10 ft. long and $\frac{3}{16}$ in. thick.

The side housings and moving slide consist of heavy rolled steel slabs of great rigidity, and the slide is of ample

depth and arranged with openings to accommodate two hydraulic cylinders. Suitable bearing pads for transmitting pressure from the hydraulic rams are welded on at the top and bottom of these openings. The desk is of welded construction.

Hydraulic cylinders, each having main and return rams for giving movement to the slide, are securely built into the framework of the machine, being supported at the front by a substantial welded steel plate bolted to both housings, and at the rear by a welded steel beam fixed to the housings with fitted bolts. The hydraulic pumping unit is fitted between the housings and behind the beams, carrying the cylinders, with the oil storage tank above.

The pumping unit is designed with a view to providing the greatest possible control of the slide, and all valves with the necessary connecting pipes are mounted adjacent to the unit. The solenoid-operated control valves are controlled by means of a foot switch at the front of the machine. A special compensating device is fitted to maintain parallelism of the slide during its travel.

Scottish Machine Tool Corporation, Ltd., 58, Victoria Street, London, S.W.1.

High Temperature Tube Furnace

THE growing need for laboratory furnaces suitable for tests and heat treatment at high temperatures, has led to a special design of furnace using a new development in silicon carbide heating elements, with this material in the form of a tube. The use of Silit rods for high temperatures has many advantages in long life and simple operation. These advantages are present in the Silit tube, with the additional important feature that uniform temperature distribution is inherent, owing to the form of the element. The new furnace (Type ST. 40/4) is suitable for operation at temperatures up to 1,500° C. and has a working tube with an internal diameter of 27 mm.

Like the Silit rod with thickened ends, the Silit tube has a larger external diameter at the ends and a central heating portion. A refractory "working tube," in which the material to be treated is placed, is fixed in the centre of the Silit tube, which is surrounded by another ceramic tube and the whole fitted into the steel cylindrical body, with suitable insulating material. The working tube is made of impervious refractory material, so that a reducing atmosphere may be used without fear of it attacking the element.

To assist accurate temperature control, the voltage applied to the heating element can be reduced by means of a tapped transformer, thus allowing the input to the furnace to be reduced so that it just maintains the furnace temperature. Tapping of the transformer secondary allows the applied voltage to be increased to compensate for the "ageing" of the element.

All the electrical equipment is housed in the bench mounting stand of the furnace, and includes the tapped transformer, tapping switch, main contactor, pilot lamp, manual power regulator and ammeter. The manual power regulator is an electromechanical device which





periodically switches on and off the furnace power supply, for intervals of time which can be pre-set. Used in conjunction with the tapped transformer, the regulator enables extremely accurate temperature control to be achieved.

Siemens-Schuckert (Great Britain), Ltd., Faraday Works, Great West Road, Brentford, Middlesex.

New Statfile Recorder

THE Statfile Recorder Model 70 mm. has been introduced by Photostat, Ltd., in response to an increasing demand for an economical method of mass recording documents and drawings. This new precision equipment is claimed to lower the cost of film recording, simplify operation procedure and, at the same time, maintain a high standard of photographic reproduction quality.

It is a complete all-metal assembly comprising a camera, camera trolley, track chassis, easel and lighting, for recording and projection on to photographic sensitized materials. The camera is equipped with a film magazine powered by an electric motor which moves the film on after exposure. This magazine is loaded with a spool of 70 mm. film which is 100 ft. in length. This will provide 300 exposures on the complete length, or, if required, short lengths of film can be cut off for processing as test negatives.

When the exposure button is pressed, the shutter is opened and after the exposure the film is automatically wound down for the next exposure. This operation can be carried out either from the main control panel on the camera trolley, or from a sub-panel at the side of the easel, so making it unnecessary for the operator to leave the easel when loading and unloading drawings and sensitized materials. The recorder has been accurately calibrated to eliminate any necessity for visual focusing. Alternative arrangements are provided for projecting from the film, either in roll form or from single-sheet negatives. The projector unit comprises a triple condenser lens assembly with a 6V. 30W. solid source

projection lamp. A Taylor, Taylor and Hobson Apotal f/9 six-inch lens is fitted to the camera, and the maximum reduction ratio is 17:1, which allows 70 mm. negatives to be made from originals up to 40 x 60 in. in size. Moreover, the quality of the projection system is such that, should the negative be enlarged back to its original size, extremely high quality definition is obtained.

The "Statfile" Recorder Model 70 mm. is equipped with two Venner synchronous timers and a Veeder-Root magnetic counter for registering the number of exposures. Two models are available; one has a 40 x 60 in. easel, and the other a 34 x 55 in. easel. This new recorder is not intended to replace the existing Statfile Recorder Model 3. The new model is ideal for mass recording of large numbers of drawings, but for the normal work of an industrial concern the half-plate recorder is the more suitable apparatus.

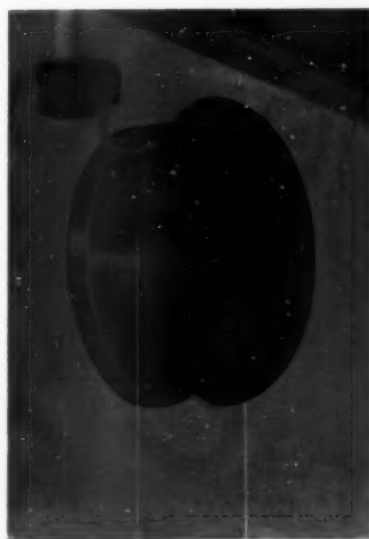
Kodak, Ltd., Wealdstone, Harrow, Middlesex.

Window Fan Development

A NEW moulded plastic impeller has been developed by The General Electric Co., Ltd., for the Company's 7½ in. Xpelair window fan. The moulded blade prevents amplification of any magnetic noise which may be present in the motor at certain speeds. At the same time the Company has produced a lightproof attachment for both the 7½ in. and 9½ in. diameter Xpelair fans, so that they may be used in X-ray and photographic darkrooms. The attachment consists of an aluminium blackout cowl which can be fitted over the bell-mouth entry of the Xpelair. This cowl excludes light completely without seriously reducing the extraction rate of the fan.

The iris shutter available with some Xpelair models is another device which is indispensable where photographic darkrooms have to be ventilated. This shutter completely closes the fan orifice when the fan is switched off, ensuring no possibility of back-draught depositing dust on plates or films being developed. Furthermore, the closed shutter safeguards against possible cooling of solution tanks, which might result from a lowering of room temperature due to back draught.

The General Electric Co., Ltd., Magnet House, Kingsway, W.C.2.



Servograph Recorder

FIELDEN ELECTRONICS, LTD., have recently introduced a high-performance low-priced recorder known as the Servograph Mark II. This versatile instrument is suitable for direct operation from pH meters, CO₂ indicators, smoke density meters, Beta gauges, tachometers, and many other uses as well as a recording voltmeter and



ammeter. The Servograph Mark II operates directly from micro-current sources; it can replace any moving coil indicating meter without imposing any additional load on the source of measurement or involving any loss of accuracy. One of the features of the new instrument is its unique principle of operation, which sets new standards in performance for graphic-recording meters. It is made in three models and is available for both laboratory and plant use.

Fielden Electronics, Ltd., Paston Road, Wythenshawe, Manchester, 22.

Tube Bending Machine

CHAMBERLAIN INDUSTRIES, LTD., manufacturers of Staffa products, have recently completed a new design of tube bending machine, manufactured under contract to their clients' special requirements. The machine is capable of 180° bends in tubes up to 3 in. nominal bore and radii in accordance with British Standards. The tubes are bent cold and unloaded, and the bending time is 25 seconds.

The machine consists of a fabricated base made from rolled steel sections and boiler plate welded together. A vertical shaft is mounted at the front end, in a roller bearing at the top and a ball bearing at the bottom, and the swinging head is keyed to the top and bottom of this shaft, which is rotated by a triplex sprocket wheel mounted on it between the bearings. The sprocket is moved by a chain and a high pressure hydraulic ram. Also mounted on the front end of the main frame is a

pressure die to take the reaction of the straight part of the tube during bending. The free end of the driving chain is attached to a smaller ram, which returns the swinging head under no load after bending. The hydraulic system is fed by a power pack consisting of a swashplate pump with a maximum delivery pressure of 5,000 lb./sq. in. driven by an electric motor and flexible coupling.

The sequence of operations during bending is first to push the tube over the mandrel, and then to wind the clamp on the swinging head to hold it against the centre former. The pressure die is then wound into the same position, and the power pack started by the push button at the control position: the main ram is actuated by pulling the hydraulic control valve lever. The sprocket is pulled round the sprocket wheel, the swinging head rotates, and the tube is drawn over the mandrel. At the end of the bend, a second hydraulic control valve actuates the retraction ram, which pulls the mandrel down the tube away from the bend. The clamp and pressure die are then wound back to allow the tube to be taken out. The movement of the first valve in the opposite direction actuates the return ram, which pulls the chain back to the starting position, returning the swinging head.

These machines can be supplied to bend any size of steam pipe or similar material up to 12 in. normal bore to radii in accordance with the British Standards specifications.

Chamberlain Industries, Ltd., Staffa Works, Leyton, London, E.10.

Arc Welding Safety Relay

PHILIPS ELECTRICAL, LTD., have introduced a low-voltage safety relay which gives welders complete protection by ensuring that at no time—except when the arc is being ignited or is burning—is a full open circuit voltage available. Official concern has recently been expressed over the number of accidents and the risk of shock, particularly when welding at altitude or in confined spaces, and with the high voltages now required by many types of electrodes, even gloves and insulated holders do not provide complete safety.

In essence, the relay—known as type PE.3100—is a voltage divider which reduces the full open circuit voltage of the power source—either A.C. or D.C.—by 50%. As soon as the electrode is brought into contact with the workpiece, the splitter device is automatically by-passed, and full voltage is available for striking an arc. A simple delay device holds the open-circuit voltage to full value for one second after the arc is extinguished, and this allows re-striking—should the arc be broken accidentally—and permits tacking of the workpiece, without re-operating the relay.

The equipment is simple to install, quite imperceptible in operation, and measures only 14 × 7 × 7 in. high. It can be fitted to the output side of any welding plant, either A.C. or D.C., up to a capacity of 500A. In the case of multi-operator equipment, the relay must be installed between each regulator and its electrode holder. A local power supply of 220V. A.C. is required; this can generally be obtained from the input panel of the plant.

Philips Electrical, Ltd., Century House, Shaftesbury Avenue, London, W.C.2.

CURRENT LITERATURE

Book Notices

MATERIAL UTILISATION IN THE METAL-WORKING INDUSTRIES

32 pp., numerous illustrations. Published by the Institution of Production Engineers, 10, Chesterfield Street, London, W.1. 5s.

OVER the past ten years the cost of materials has followed an upward trend and accounted for an increasing percentage of the total factory cost. An analysis of overheads also reveals a high material content as, for example, in the case of paper, oils, grease, degreasing and cleaning detergents, etc. It is becoming accepted practice for production engineering to begin at the design stage, and it is here that co-ordination with the design staff can ensure that material removal operations are reduced to the economical minimum.

This publication is a Report of a Sub-Committee of the Research Committee of the Institution of Production Engineers, which was set up to investigate the extent to which British industry is making the best use of materials, to discover what proportion is converted into useful products, and to see if ways can be found to increase that proportion. In this first Report, the Sub-Committee has confined its investigations to the metal-working industries and to metal working. The Report is based on a large number of case studies which were collected from industry, mostly with the help of Working Parties set up by various Sections of the Institution; it is set out in three main sections: (a) a general survey of the present position; (b) a large number of illustrated case studies; and (c) conclusions and recommendations. The aim of the Sub-Committee has been to provide a publication of direct use to the production engineer, with the information set out in a brief and easily digested form. It is the belief of the Sub-Committee that much can be done by industry to improve the effective utilisation of material, and an examination of this Report should give food for thought.

METALS HANDBOOK, 1955 SUPPLEMENT

208 pp., 214 tables, 256 charts and 411 illustrations. Published by the American Society for Metals, 7301 Euclid Avenue, Cleveland 3, Ohio. \$6.00 to non-members.

THE technical committees of the American Society for Metals have completed the Second (1955) Supplement to the Metals Handbook. As with the 1954 Supplement, multiple authorship gives authoritative coverage of selected subjects. Nineteen committees with a total of 179 author members, all of whom are recognised experts, contributed to this volume.

Although the Supplement encompasses a wide range of metal-working subjects, these are grouped conveniently into four categories: metals and applications, design and application, processing and fabrication, and testing and inspection. Of the 21 subjects reported on, at least two-thirds are of direct concern and interest to the metallurgist. Thus, since no function is more intimately associated with the role of metallurgists than selection of metals, the Supplement contains six such articles. These pertain to aluminium castings, grey iron, sheet

steel for formability, material for press forming dies, electroplated coatings, and stainless steels for chemical process applications. Each of the articles aims at presenting a complete survey of the important factors affecting selection. Completeness is achieved because the articles represent the cumulative knowledge of the committee of experts writing on the subject. For example, in the article on selection of sheet steel for formability, a severity classification system that correlates the severity of forming with the mechanical properties of the steel is introduced as a means of selecting the most economical steel. It is unlikely that an article of this scope could have been organised by a single author. Some idea of the thoroughness devoted to this subject may be indicated by the fact that 97 illustrations, 17 tables and 17 charts supplement the copy to explain this concept of severity classification.

The articles on selection, as well as those in the other categories, consider two topics that are seldom found in the usual technical article. Cost is one of these, and is dealt with in 12 of the articles. The article on cost of metal cleaning, is devoted entirely to this aspect of the subject. Another significant contribution is the reporting of engineering data as distribution or ranges for samples from production items representing many heats. Such information is more useful than typical or nominal values.

The four articles on heat treating refer to induction hardening and tempering, flame hardening, gas carburising, and heat treatment of tool steels, as well as the articles on the closely related subjects of carbon restoration and carburising atmospheres. The division of the gas carburising article into two parts, one on commercial practice and the other on application of equilibrium data, is a helpful device. Although all of these articles, as well as those on selection of welding electrodes and analysis of cleaning costs, are a significant contribution to metallurgical literature, the articles on induction treating and on gas carburising form a "blue-print" for practical operations.

The section on testing and inspection has articles on macro-etching of iron and steel, creep and creep rupture tests, and radiography. Here again the approach that seems to have been stressed is one of practicability.

In view of this apparent aim to present only useful engineering information, the 1955 Supplement should be very useful to the majority of metallurgists whose main concerns are utilitarian rather than scientific.

MECHANICAL WORLD YEAR BOOK

1956 Edition. 326 pp. Emmott & Co., Ltd., 31 King Street West, Manchester, 3. 4s. 6d. net.

This year the Mechanical World Year Book presents an entirely new section on gas turbines. Its forerunner served a useful purpose in recent years by providing a fundamental thermodynamic approach, but now that experience of gas turbine design has accumulated, it is thought that a more advanced account of current practice is required. Accordingly, a concise section on design procedure has been specially prepared. This presents data and detailed methods for use in dealing with the principal components. Additional or revised material

appears in the sections or tables on materials, power plant, limits and fits, keys, and cutting speeds and feeds, and an addition has been made to the tables giving the properties of the circle.

ELECTRICAL YEAR BOOK

1956 Edition. 362 pp. Emmott & Co., Ltd., 31 King Street West, Manchester, 3. 3s. 6d. net.

THE applications of electronics increase almost daily: thermionic valves and their accompanying equipment are now used in spot welding, high frequency generation, induction and dielectric heating, control instruments, etc.—to mention but a few outside the radio and television field. A new section in the 1956 edition of the Electrical Year Book presents a precise account of electronic fundamentals and methods, illustrating these by reference to the more appropriate of the new applications. In the section on electric lighting, new matter has been included on the quick-start fluorescent lamp, giving information on circuits and arrangements for dimming.

Trade Publications

THE suitability of high-purity aluminium for fully-supported roofing and flashing is becoming more and more widely recognised as old and new buildings, some of them of historic importance and all built to last for generations, are given this form of protection. The characteristics of Noral High-purity Aluminium and useful notes on its application are given in a new eight-page folder, entitled "Noral High-Purity Aluminium for Roofing and Flashing," issued by Northern Aluminium Co., Ltd. This material is of 99.7% purity and fully annealed: it forms as easily as copper though not as easily as lead, while being much cheaper than either and having comparable durability.

THE complete range of the Company's wrought aluminium mill products is presented in a new eight-page brochure "Aluminum Products" prepared by Harvey Aluminum, 19200 S. Western Ave., Torrance, California. Illustrations and text describe extruded shapes, structurals, machining stock, drawn tube, forging stock, press forgings, impact extrusions, screw machine products, and heavy press extrusions. Included are tables pertaining to standard manufacturing limits for extrusions, standard tolerances, and properties and typical uses for various aluminium alloys.

FOLLOWING the recent amalgamation of the activities of The Quasi-Arc Co., Ltd., and Fusarc, Ltd., a new comprehensive catalogue (TC.845) has now been issued by Quasi-Arc, Ltd., of Bilston, Staffordshire, giving details of manual and automatic welding equipment, installations, electrodes and supplies.

THE October issue of *The Nickel Bulletin* includes a series of interesting items on cast iron, covering thermal-shock resistance, the properties of low-expansion nickel-alloy irons and oxidation-resistance of high-alloy types. In connection with high-temperature materials attention is directed to the announcement of a new member of the Nimonic series, Nimonic 100, which can be used at temperatures higher than those permissible for any other alloy of the group. Among abstracts relating to gas-

turbine materials is a study of the relation between static and fatigue properties at elevated temperatures, and a report on the influence of vanadium pentoxide on the scaling of alloys at high temperatures. References to stainless steels in chemical engineering include applications in pickling equipment, dyeing plant, pulp-bleaching equipment and other branches of the process industries. The increasing importance of such materials in structural engineering is demonstrated by a report on fundamental research which is in progress as a basis for formulating a design specification for the hardenable 17-7 chromium-nickel grade. Copies are obtainable from: The Mond Nickel Co., Ltd., Publicity Department, Thames House, Millbank, London, S.W.1.

LEAFLET No. MFD.1/3.55/08, issued by the Metal Finishing Division of The Pyrene Co., Ltd., Great West Road, Brentford, Middlesex, features Detac No. 1. This is a water soluble material for the treatment of the re-circulating water in water-conditioned paint spray booths. Its function is to denature the overspray paint and, by removing all stickiness, to prevent the adhesion of the overspray paint to reservoir walls, eliminator pipes and pumps, thus greatly reducing the labour required to maintain spray booths in a clean condition. Detac No. 1 can be used in all types of booth where the water conditioning system is of the re-circulating type.

WE have received from Firth Brown Tools, Ltd., Sheffield, an illustrated brochure dealing with Zeelock serrated blade cutters with Speedicut high-speed steel blades and tough alloy steel bodies. Each blade is held in position by interlocking serrations on itself and the body, and is locked solidly by means of a Z-shaped wedge. The step on the back of the wedge is milled at such an angle that when the blade is adjusted for wear by being moved out one serration, it is also moved forward to take up any wear on the face.

THE November issue of *Hilger Journal* features a number of interesting articles, among which is one describing the use of the Hilger medium quartz spectrograph with its direct-reading attachment in metallurgical analysis. The major part of the article is taken up by a description of the instrument, but reference is made to the accuracy and reproducibility of results.

DESIGN data on the entire range of Nimonic alloys, including preliminary details of the recently introduced creep-resisting material Nimonic 100, are contained in a new edition of "The Nimonic Alloys," available from Henry Wiggin & Co., Ltd., Wiggin Street, Birmingham. 16. Extensive revisions have been made in this booklet in the light of creep and fatigue test results obtained since the earlier edition was published. For example, 10,000-hour creep data for Nimonic 90 and 95 are included for the first time and the fatigue properties of Nimonic 80A at 700°C. and 750°C. are indicated by means of Gerber diagrams. Long-time creep testing of Nimonic 90 is giving some interesting results, a test piece stressed at 5 tons/sq. in. and heated continuously at 750°C. having shown a creep strain of less than 1.0% in its first 15,000 hours. Other information given on the Nimonic series includes the specified compositions, hardness ranges, physical properties, recommended heat treatments, short-time high-temperature tensile properties and results of torsion tests.

LABORATORY METHODS

MECHANICAL • CHEMICAL • PHYSICAL • METALLOGRAPHIC

INSTRUMENTS AND MATERIALS

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The Determination of Zinc in Copper Alloys

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A chromatographic method is described for the separation of zinc in the range 1-40% from all normal types of copper-base alloy. The separated zinc is determined by titration with disodium ethylene diamine tetra-acetate (E.D.T.A.). The conditions for accurate determination of the zinc have been investigated, as has the effect of various elements on the separation and titration.

THE difficulty experienced in the separation of zinc in copper and other alloys is well known. The established sulphide separation method¹ is long and tedious, and, unless conditions are carefully controlled, quantitative separation is not achieved: the ferrocyanide determination of separated zinc has also led to much controversy². For the final determination of zinc, several methods are used, and the application of disodium ethylene diamine tetra-acetate (E.D.T.A.) for this purpose is now finding much favour³⁻¹².

Cellulose chromatography and ion exchange techniques are now widely applied in inorganic analysis^{13, 14}, and Wells has recently reviewed developments in this field¹⁵. Miller and Hunter¹⁶ separated zinc from certain other elements by means of ion exchange, but the application of this technique is somewhat limited for a wide range of copper-base alloys. Bishop and Liebmann¹⁷ have separated small quantities of zinc and aluminium from tin-lead alloys by cellulose chromatography, prior to polarographic determination, and these workers have also separated zinc from tin, aluminium, nickel, lead, manganese, bismuth, cobalt, copper and iron.

In view of the foregoing, it was decided to attempt a chromatographic separation of zinc from copper alloys, followed by complexometric determination of the zinc by E.D.T.A.

Measurement of Zinc

In using E.D.T.A. with Eriochrome Black "T" as indicator for the determination of zinc, many varied ammonium hydroxide-ammonium chloride concentrations have been suggested for the formulation of buffer solutions. Kinnunen and Merikanto³ recommended one comprising 350 ml. ammonium hydroxide (sp. gr. 0.880) and 54 g. ammonium chloride, made up to one litre with distilled water. Using this system on a micro-titration of a pure zinc solution, very poor end points were obtained, and various other suggested systems gave similar results. It thus became necessary to investigate the buffer system more closely.

INVESTIGATION OF BUFFER SYSTEM

0.1 g. zinc was titrated with 0.1 N E.D.T.A., using a micro-burette reading to 0.001 ml., the pH values of

TABLE I.—EFFECT OF RATIO OF AMMONIUM CHLORIDE TO AMMONIUM HYDROXIDE ON THE END-POINT IN THE TITRATION OF ZINC WITH 0.1 N E.D.T.A.

Ammonium Chloride (%)	Ammonium Hydroxide (%)	pH	Nature of End-Point Colour Change
NH	1-4	11.30-11.60	End-point change good
NH	5-10	11.60-11.70	Quality of the end-point progressively deteriorated
1	1-4	9.40-9.95	End-point change good
1	5-10	10.05-10.40	End-point change excellent*
1	15-25	10.60-10.85	End-point change good
1	30-40	10.95-11.16	End-point change poor
2	1-30	9.12-10.60	End-point change poor
5	1-8	8.65-9.80	End-point change poor
5	9-70	9.60-11.00	End-point change very poor

* The end-point colour change was much clearer and sharper than with any other ammonium chloride-ammonium hydroxide system. The pink colour was maintained until the slightest excess of E.D.T.A. produced a pure blue colour.

the solutions being determined electrometrically with the aid of a glass electrode (linear over pH range 1-14). From the results obtained (which are set out in Table I) it was observed that the ammonium chloride concentration is critical, and that the pH value is not the only controlling factor of the buffer, since solutions of the same pH value, but containing various ratios of ammonium hydroxide to ammonium chloride, gave poor end points if the ammonium chloride concentration exceeded about 1%. The buffer chosen contained 80 ml. ammonium hydroxide (sp. gr. 0.880) and 10 g. ammonium chloride per litre.

In the following experiments, the zinc range covered was from 0.15 mg. to 8.0 mg., and, using a burette reading to 0.001 ml., 30 determinations of zinc gave the following results:—

1.0 ml. 0.1 N E.D.T.A. \equiv 3.26 mg. zinc
Standard Deviation = \pm 0.0236 mg.
Coefficient of Variation = 0.73%

INFLUENCE OF CHROMATOGRAPHIC SOLVENT ON TITRATION

Bishop and Liebmann¹⁷, after eluting the zinc from the cellulose column, evaporated the eluate to dryness, destroyed organic matter with perchloric acid, and separated the iron present by ammonium hydroxide precipitation. However, it was decided to investigate

TABLE II.—EFFECT OF VARIOUS ELEMENTS ON THE TITRATION*

Element	Effect on Titration
Aluminium	Up to 5% has no effect
Antimony	Up to 50% has no effect
Arsenic	Up to 50% has no effect
Tin	Up to 60% has no effect
Bismuth	Up to 4% has no effect
Lead	Trace interferes
Cadmium	Trace interferes
Copper	Trace interferes
Manganese	Trace interferes
Nickel	Trace interferes
Iron	Does not interfere directly, the bulk of precipitate being the controlling factor

* Calculations are based on an original sample weight of 0.10 g.

the titration of the zinc in the presence of the butanol solvent with buffer present. The experiment revealed that not only was it possible to titrate the zinc in the presence of the butanol, but the presence of this solvent assisted the end-point by making the colour change more pronounced, and it was found that the reproducibility was improved.

Using a burette reading to 0.02 ml., a series of 14 determinations under these conditions gave the following results:—

1 ml. 0.1 N E.D.T.A. = 3.23 mg. zinc
Standard Deviation = ± 0.0104 mg.
Coefficient of Variation = 0.32%

EFFECT OF IRON ON THE TITRATION SYSTEM

In the chromatographic separation, zinc moved down the column first, followed by a yellow iron band which acted as a marker. However, it was found that the tail end of the zinc band was over-lapped by the iron band, and, therefore, part of the iron band had to be eluted in order to ensure complete zinc extraction.

The question arose as to whether iron would interfere with the titration.

Experiments on the direct titration of zinc and iron in buffered solution, with butanol absent, gave rise to high results and poor end-points, even when the iron was only present in small amounts. The same titration when carried out with butanol present revealed that it was possible to titrate the zinc without any interference from the ferric hydroxide. Thus, in the chromatographic separations, if part of the iron band was allowed to break through after the zinc, and the eluate reduced in volume to about 10–20 ml., the solution could be titrated without any difficulty, after the addition of approximately 50 ml. of buffer solution.

It was observed that an effect on the end-point colour change was registered, depending upon the quantity of iron eluted, in that instead of the change being pink-blue, the change was pink through grey near the end-point to a bright green. This change was distinct and occurred with the slightest excess of E.D.T.A. It was found that up to 10% iron on 0.1 g. sample could be tolerated in the titration, but beyond this, the bulk of ferric hydroxide precipitated was such that its colour made it very difficult to see the end-point change. If the precipitate was allowed to settle, the colour change could still be seen. The quantity of the precipitate does not interfere with the chemical action of the titration in any way.

The effect of the amount of butanol solvent was investigated by adding from 10 to 100 ml. to the buffered titration system containing 5 mg. of iron. It was found that up to 100 ml. of the solvent could be tolerated without interference.

EFFECT OF VARIOUS ELEMENTS

Various elements were investigated as to their effect on the titration, and the results are set out in Table II.

Chromatography of Zinc

For quantitative work, all chromatographic separations were carried out on cellulose columns, 7 in. long \times $\frac{3}{4}$ in. diameter, prepared from Whatman cellulose powder for chromatography. The Pyrex glass column was pre-treated with D.C.200 Silicone fluid to produce an anti-wetting surface as recommended by Burstall *et al*¹⁸.

For actual separations, metallic chloride solutions absorbed on a cellulose pad were applied to the top of the column and eluted with a solution consisting of four parts 20% v/v hydrochloric acid and 96 parts *n*-butanol (by volume). Under these conditions, zinc first moved down the column followed by iron, which acted as a marker, then copper, tin, lead, aluminium, nickel, manganese, cobalt and bismuth¹⁷. The technique employed for all the experimental chromatographic work was as described below under "Recommended Procedure."

Synthetic mixtures were prepared from chloride solutions (where possible) of iron^{III}, manganese, magnesium, arsenic^V, antimony^V, copper, aluminium, lead, bismuth^{III}, tin^{IV} and cadmium. The volume of sample was reduced to a minimum, then absorbed on cellulose powder and loaded on to the column. Each synthetic mixture contained 10 mg. zinc. Extraction of zinc was achieved quite readily from simple mixtures (e.g., zinc, iron^{III}, copper, nickel and tin^{IV}) but from complex mixtures poor separation was obtained. This was considered to be due to overloading of the column (both in weight and in volume of sample added), and on further investigation it was found that 0.1–0.15 g. of sample could be loaded on to a 7 in. \times $\frac{3}{4}$ in. diameter column, to yield good separation. This weight of sample should preferably be contained in a volume of 2 ml.

Quantitative determination of the zinc gave slightly high results, and further investigation revealed that impurities in the butanol were responsible. This was overcome by distilling the butanol or using AnalaR grade. Having achieved a separation of zinc from a series of elements, it was decided to use standard copper alloys (B.C.S. Bronze A—zinc = 1.86%; and B.C.S. Bronze B—zinc = 33.9%), weighed out in various proportions to produce alloy mixtures with zinc contents ranging from 1.86% to 33.9%, for the purpose of zinc recovery investigations.

2.5 g. of mixed sample were dissolved in *aqua regia*, the excess acid boiled off, and the solution diluted to

TABLE III.—ZINC RECOVERY USING B.C.S. MIXTURES*

Sample Number	Calculated Zinc Added (%)	Zinc Found (%)			
		A	B	C	D
1	33.90	33.4	33.10		33.40
2	30.69	30.50	30.20	30.40	30.40
3	27.49	27.30	27.50	27.20	27.40
4	24.29	24.00	24.00	23.80	23.80
5	21.08	20.20	20.60	21.00	20.90
6	17.88	17.65	17.60	17.55	17.90
7	14.67	14.50	14.50	14.60	14.65
8	11.47	11.55	11.50	11.55	11.60
9	8.27	8.25	8.25	8.25	8.25
10	5.06	4.90	4.97	4.90	4.90
11	1.86		1.82	1.80	1.84
12	Bronze Alloy B.C.S. 207 zinc—2.53			2.53	

* The groups of standards were run as four separate investigations, viz., A, B, C and D.

25 ml. : 1 ml. was then transferred to the column after absorption on cellulose powder. The results obtained are shown in Table III. From these results it is apparent that good recovery of zinc is obtained within the range 1-40%, with good reproducibility. In order to evaluate the range of alloys to which the method is applicable, mixtures of B.C.S. alloys and pure metals (where possible) were prepared and investigated. The results obtained are shown in Table IV from which it is seen that large percentages of elements normally encountered in copper-base alloys can be tolerated without interference.

Recommended Procedure

From the work described above a single procedure has been developed for the separation and determination of zinc over a range of approximately 1-40% in most types of copper-base alloys. This procedure is used without any modification whatsoever. The total time for separation and determination for a batch of about six samples is of the order of two to two-and-a-half hours. Initial equilibration of the column requires about one to one-and-a-half hours, for 100 ml. of solvent flow. Details of the procedure are given below.

APPARATUS

The absorption apparatus consists of a glass tube about $\frac{3}{4}$ in. diameter and 12 in. long, the upper end being widened to form a funnel to allow easy transfer of the material to the tube. The lower end of the tube is narrowed to a $\frac{1}{4}$ in. diameter outlet, closed by a short length of polythene tubing and screw clip. Inside the tube at the base, rests a small glass bead to support the cellulose. The inside surface of the glass tube is treated with 2% D.C.200 Silicone in carbon tetrachloride solution to produce strong water-repellent properties.

REAGENTS

- (1) *Solvent*—four parts 20% v/v hydrochloric acid and 96 parts purified butanol.
- (2) *E.D.T.A. Solution*—0.1 N disodium ethylene diamine tetra-acetate (18.75 g./litre). 1 ml. of this solution is approximately equivalent to 3.20 mg. zinc.
- (3) *Buffer Solution*—80 ml. ammonium hydroxide (sp. gr. 0.880) + 10 g. ammonium chloride made up to 1 litre with distilled water.
- (4) *Indicator*—0.5% Eriochrome Black "T" in 30% iso-propyl alcohol in water.
- (5) *Ferric Chloride Solution*—5% w/v solution in dilute hydrochloric acid.
- (6) *Standard Zinc Solution*—1 ml. = 10 mg. zinc.
- (7) *Cellulose*—Whatman standard grade for chromatography. This cellulose was found quite satisfactory and needed no preparation before use.

PREPARATION OF COLUMN

Mix cellulose powder and solvent in a beaker to produce a pulp slurry and transfer to the column. Allow the cellulose to gravity pack, breaking up any aggregated pieces with a glass rod flattened at one end to form a plunger of diameter slightly less than that of the tube. When the cellulose has packed evenly, gently push it down with the rod to produce a moderately tight column 7 in. high.

EQUILIBRATION OF COLUMN

Allow 100 ml. of solvent to pass through the column in order to equilibrate the cellulose with the solvent.

TABLE IV.—EFFECT OF HIGH CONCENTRATION OF VARIOUS ELEMENTS ON THE PROCEDURE

Element	Amount Present (%)	Zinc Added (%)	Zinc Found (%)	Relative Error (%)
Lead	15	1.86	1.84	-1.07
Antimony	5	1.86	1.84	-1.07
Nickel	20	1.86	1.84	-1.07
Magnesium	10	1.86	1.84	-1.07
Manganese	10	1.86	1.84	-1.07
Bismuth	5	1.86	1.84	-1.07
Aluminium	20	33.90	33.70	-0.59
Tin	30	23.73	23.60	-0.55
Chromium	10	30.51	30.30	-0.68
Arsenic	5	1.86	1.84	-1.07
Cadmium	5	32.21	33.00	+2.45
Cadmium	2.5	33.10	33.40	+0.90

PROCEDURE

Prepare a cellulose column as described above and equilibrate. Adjust the solvent level in the column until it coincides with the top of the cellulose.

Dissolve 0.1 g. of sample in *aqua-regia*, add 1 ml. of 5% ferric chloride solution and evaporate almost to dryness. Take up the sample solution with a minimum volume of solvent, and add sufficient cellulose pulp to the beaker to absorb the solution completely.

Stir the mixture thoroughly with a glass rod. Transfer the wad containing the absorbed sample to the top of the column, finally washing into the column with not more than 10 ml. of solvent from a wash bottle. Break up the pulp containing the sample with a small glass plunger and gently press down to form a continuation of the original column of cellulose.

Remove the clip from the bottom of the column and allow the solvent to run into a 250 ml. beaker, until the level of the solvent coincides with the top of the cellulose column. Add a further 10 ml. of solvent and allow this to flow to the same stage. Now add solvent to the column to ensure continuous elution, until the eluate in the beaker has a distinct yellow iron colour, but do not allow all the iron band to break through. Boil down the eluate to about 10-20 ml., cool, add 50 ml. of buffer solution, then about 6-10 drops of Eriochrome Black "T" indicator and titrate with 0.1 N E.D.T.A.

This solution should be previously standardised against standard zinc solution with 20 ml. of solvent, 5 mg. iron and 50 ml. of buffer solution added.

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High Resolution Autoradiography

Wet process autoradiography has been adapted for use with metallographic specimens. Under favourable conditions segregation of particles as small as 1 micron in diameter, and with an inter-particle distance of less than 10 microns, can be studied. Attention is drawn to the advantages and limitations of the technique.

AUTORADIOGRAPHY has been used only to a limited extent in metallurgical studies, largely because of the difficulty of obtaining the high resolution required in many investigations. A wet-process autoradiographic method, developed in other fields, has now been successfully adapted to the location of suitable *beta*-particle-emitting isotopes in the microstructure of metallurgical samples. Demonstrations have shown that autoradiographs can be produced, which will resolve radioactive areas separated by less than 10 microns.

This work was carried out at the University of Michigan and is reviewed by George C. Towe, Henry J. Gomberg and J. W. Freeman in a report published by the U.S. National Advisory Committee for Aeronautics as Technical Note 3209. The report is available on loan from TIDU, Cunard Building, 15, Regent Street, London, S.W.1 (reference NACA TN 3209).

The heat resistant alloys which have been developed for the severe temperature and stress conditions of modern aircraft propulsion systems generally have complex microstructures. Research on these alloys is often handicapped because the metallurgist is unable to determine the composition of the segregated microconstituents through which the properties of the alloys can be drastically modified by metallurgical treatments. Similarly, the metallurgist often cannot determine where alloying elements are located in the microstructure. Such information is required for the understanding necessary for good control of properties and the efficient utilisation of alloying elements.

Autoradiographs of microstructures using radioactive isotopes of the alloying elements offer considerable promise as a means of partially determining the composition of complex microconstituents. To enable the best use to be made of it, the technique should be capable of showing the presence of radioactive elements in microconstituents at least as small as 1 micron and spaced not more than a few microns apart. Wet-process autoradiography, as developed in 1949 by Dr. Henry J. Gomberg at the University of Michigan, to attain the same objective in biological studies of tissues, offered considerable promise for metallurgical studies. Work was therefore started to adapt this method for metallurgical purposes.

Development of Technique

The first stage of the high-resolution process described is the preparation of a collodion film on the surface of a polished and etched metallographic sample containing radioactive alloying elements. The collodion film contains soluble halides which form insoluble silver halides when immersed in a silver nitrate solution. While the silver halide forms, it is subject to ionisation by the radiation from the metallurgical sample, reducing a very small amount of the silver halide to silver. The radiation-affected silver halide in the collodion emulsion is then developed and fixed. When properly carried out,

the developed silver grains are located directly over the radioactive region and thereby locate the site of the activity.

High-resolution autoradiography requires that the emulsion be very thin and in intimate contact with the sample surface. Interpretation of the autoradiographs is facilitated by keeping the emulsion in place on the specimen during and after photographic processing. It is almost a necessity, and certainly desirable, that the microstructure of the metal should be visible through the autoradiograph.

In 1949 the best autoradiographs were obtained by placing metallurgical sections in contact with dry photographic emulsions. The resulting autoradiographs had to be compared separately with the metal structure, and the highest magnification possible was of the order of 50 diameters.

In attempting to adapt the wet-process technique to metallurgical samples, one problem which required solution was the corrosion of the metal surfaces: suitable protective layers had to be developed. Finally, optimum emulsion processing conditions had to be established. Carburised iron samples and radioactive nickel, plated on platinum, were adopted as standard radioactive sources in the development work, and were used to illustrate the results of the process. The specifications for the radioactive samples for successful autoradiography were also evaluated.

Considerable effort was devoted to the improvement of the collodion "emulsion" layer, and its thickness was reduced to approximately 4 microns. Various organic and inorganic sensitizers were added with no noticeable effect. The collodion layer is heavily loaded with silver bromide, so that the samples were well covered by the detecting crystals, the silver bromide grains being approximately 0.2 micron in diameter. The detecting layer is formed and remains directly on the surface of the protective layer, and the autoradiographic image has never been observed to be displaced from the source of radioactivity.

Many different developing agents were investigated, the agent recommended being a 4% aqueous solution of ferrous sulphate. The effect of variations in development time and temperature was also studied. Background photographic fog was greatly reduced by a cold exposure (2°C.), and by this and other methods the control achieved over background fog was sufficient to allow background silver grain counts of less than 1,000 grains/sq. mm. Emphasis is placed on the importance of keeping dirt and other contaminations from the metallographic mount and from the processing solutions, and also of using chemically pure or analytical grade chemicals.

Properly carried out, an autoradiograph is produced in place on metallographically polished and etched specimens with the microstructure and the autoradiograph visible at the same time. Such autoradiographs can readily be examined at magnifications as high as

1,000 diameters. They can also be viewed satisfactorily under low magnification (e.g., $\times 25$). Under favourable conditions the presence or absence of radioactive elements in the segregated constituents of the microstructure can be detected when the distance of separation of the particles is less than 10 microns. Under proper conditions of intensity of radioactivity in the tracer element, composition of the segregated constituent, and exposure time, the process will work for segregated particles as small as 1 micron in diameter. Grain-boundary segregations can be studied autoradiographically provided (1) that sufficient activity can be imparted into the grain-boundary constituents; (2) that the grains are larger than 10 microns in diameter; and (3) that the concentration gradients are sufficiently large.

Advantages and Limitations

Wet-process autoradiography, as developed at the University of Michigan, should thus be a useful tool for metallurgical research. It offers the following major advantages:—

- (1) High resolution for *beta*-emitting isotopes. There are no *beta* autoradiographs in the published metallurgical literature which have shown resolution of better than 10 microns.
- (2) Perfect registry of the autoradiograph over the microstructure under conditions convenient for comparison of the structure with the resulting autoradiograph at high magnification under the microscope.
- (3) Satisfactory procedures for controlling background fog.

On the other hand, the process also has certain disadvantages. One restriction, which is common to all tracer studies, is the need for a certain amount of specialised equipment and trained staff for the proper handling of radioactive substances. However, this need not be considered a serious obstacle, since many laboratories are being equipped and staffed to handle such materials.

There are also several limitations which are inherent in autoradiography itself. These may be summarised as follows:—

- (1) It is unlikely that autoradiography will ever provide the answer to all segregation problems. There are many radioisotopes available for tracer studies, but some elements (e.g., titanium and nitrogen) do not have radioisotopes suitable for such studies. Titanium and nitrogen are available only as very short-lived materials, the half lives being less than a few minutes.
- (2) Other elements are unsuitable for highest resolution work because of the quality of their radiation. Phosphorus-32, for example, has a very penetrating *beta* particle, while cobalt-60 has penetrating *gamma* rays emitted with its *beta* particles. Though both phosphorus-32 and cobalt-60 can be used in autoradiographic studies, the resolution obtained will in general be inferior. In the autoradiography of bulk metal samples the highly penetrating radiations create a serious problem. A radioactive particle, located beneath the surface of the metal and therefore invisible microscopically, will be able to activate the photographic emulsion in the vicinity. Only by repeating the autoradiograph can the investigator determine whether such

a photographic image is in reality due to radiation from a subsurface source or merely a chance accumulation of fog grains. The apparent size of a segregate particle may also be distorted by similar subsurface radiation effects.

- (3) Many segregation problems will be made much more difficult by the existence of shallow concentration gradients. No attempt has been made to evaluate the requirements for concentration gradients, but, in general, it can be said that the sharper the gradient the better is the chance of observing segregation autoradiographically.
- (4) The present state of the art requires that the segregate particles be several microns apart and have activities of several disintegrations per hour for favourable autoradiographic inspection.
- (5) The present techniques require the use of a protective plastic layer about 1 micron in thickness. If the thickness of the layer could be reduced materially, and if the radiation-sensitive layer could be thinned down to perhaps 1 or 2 microns, still higher resolution than that achieved at Michigan might be expected.

Another restriction, which is peculiar to the wet process, is concerned with length of exposure. The thin Vinylite layer protects active metal specimens for only about a day. Repeated dipping into the 2% VYNS solution (with intermediate heating) will build up the Vinylite layer and permit longer exposures, but only at the expense of high resolution.

In general, the autoradiographic image is easily correlated with some structural characteristic in the metal. Under these conditions, interpretation presents no great problem. As previously indicated, however, it is possible for chemical or physical action to induce a photographic effect. The chemical effects might be caused by interaction between the photographic chemicals and the sample itself. Chemigraphs which very closely resemble autoradiographs in appearance have been prepared on non-radioactive samples.

Other investigators have been able to prepare photographic reproductions of metal surfaces by applying mechanical pressure to photographic emulsions. Caution must be used in interpreting any autoradiograph prepared in a manner which might have introduced mechanical effects. The use of a non-radioactive control sample greatly minimises the possibility of misinterpretation.

Steel Supplies

(continued from page 1)

finance, for, to attain a production of 28 million tons in 1962, a continuing expenditure of £80-120 million a year would be necessary, on the basis of current prices. The industry's capital programme since the war has been financed from internal resources to the extent of about 50%, and if this figure is to be maintained, or, perhaps, exceeded, there must be an enlargement of the net income accruing to the industry, which has only increased threefold since 1938, as compared with the fourfold increase in the steel-consuming industries. A closer correspondence of its earning powers with those of its consumers is necessary if it is to be able to provide the capacity for a sustained rate of expansion in the use of steel.

Determination of Nickel, Chromium and Molybdenum using the Spekker Absorptiometer

By J. Winning, D.R.T.C., A.I.M., and S. Miller

Albion Motors, Ltd., Glasgow.

The reagents used in the improved methods described here are all everyday inexpensive chemicals, and the authors claim a considerable increase in speed and a substantial saving in cost compared with those using perchloric acid or silver nitrate. Moreover, the absence of heavy fumes improves the laboratory atmosphere appreciably.

SINCE the introduction of absorptiometric methods, and more especially since the "Spekker" instrument became almost a standard piece of laboratory equipment, the various users have been engaged in developing "direct" time-saving procedures. The mercury-vapour lamp, with its narrow spectral transmission proved to be a considerable advance in technique, since it largely eliminated the need for tedious and time consuming "blanks." In a busy routine laboratory, handling large numbers of steel samples daily, the adoption of the mercury lamp permitted a material increase in output to be achieved without loss in accuracy. Within very wide limits, steels of the same general type could be rapidly and confidently analysed on one calibration. The practical elimination of interference by the "blank" meant in most cases the colour developed was strictly proportional to the amount present and followed a straight-line relationship over the whole calibration, provided the proper colour filters were chosen. There was thus little room for ambiguity in constructing the calibration graph, since the line runs through the origin and can be laid down with a ruler.

On the chemical side, attempts to avoid the use of silver nitrate as a reagent early led to the adoption of perchloric acid. This technique, now widely used, will convert chromium into the yellow dichromate under suitable conditions, without the use of embarrassing catalysts such as silver salts. As is well-known, the use of silver nitrate-persulphate methods for producing the dichromate colour can be seriously in error, because of the faint opalescence which is so easily developed by even minute traces of chlorides.

Perchloric acid might have been the ideal reagent had it not suffered from a bad reputation as an explosive substance. More than one laboratory has had experience of explosions in the flues of fume-cupboards where this substance is freely used, and in some of the older laboratories, where wood enters into the construction, it could conceivably become a decided fire risk. Chemically speaking, it is not a very good solvent acid when used alone, and of course, has to be taken to the fuming stage before it can change trivalent chromium to the hexavalent form. For the same reason, chlorides must be absent or the chromium will be lost as the volatile chromyl chloride. Thus the choice of additional solvents is rather limited when dealing with stainless steels and other materials of this type, which are quite insoluble in perchloric acid alone. Finally, the question of cost must be considered. In the author's opinion, perchloric acid would require to show much greater advantages than, in fact, it does, to justify its high cost. At something like

90s. per litre, it can easily become a major item in the economics of a large laboratory.

The authors were impressed by the simplicity and almost universal application of what has now come to be known as "Spekker Acid," (150 ml. each of sulphuric and phosphoric acids to 1 litre water) and felt that this might replace perchloric acid if a sufficiently powerful oxidiser could be incorporated with it. The old Vignal's method for chromium suggested itself as a means of developing the chromium colour directly, but, unfortunately, under the conditions necessary for use in the absorptiometer, the reaction did not appear to go to completion. Potassium permanganate alone is evidently not powerful enough, but it was found that permanganate and ammonium persulphate together could oxidise the chromium completely, and, furthermore, the excess permanganate colour could easily be discharged with a few drops of hydrochloric acid, leaving the chromium ready for direct measurement. The remainder of this solution can then be used for estimation of nickel and molybdenum, and any other elements, using normal methods.

Nickel determinations on a suitable aliquot of the above solution, containing hexavalent chromium, presented no difficulties whatever, and the normal method employing the oxidised glyoxime colour was followed. Molybdenum, however, presented some difficulties because of colour fading, and clearly required some stabilising reagent to be present. Perchloric acid has been advocated for this function, and appears to work quite well, although the chemistry of the reaction is obscure. This reagent cannot, of course, be used in the presence of potassium salts, since the solution clouds up with insoluble potassium perchlorate, and in the present case, a fair amount of potassium permanganate had been introduced previously. (For the same reason, manganese must be estimated on a separate sample by orthodox methods.) It was thought that a fairly high acid concentration with some halogen acid to stabilise the stannous chloride might yield useful results, and after many trials it was found that bromide in strongly acid solution both stabilised the final colour and greatly accelerated the reaction. The reduction of iron appeared to go to completion even when molybdenum was low or absent.

According to the class of steels being handled, the dilutions of the various aliquots must be adjusted to bring the colours, finally developed, into the range of the instrument. In the present case, the class of materials most frequently encountered were low-alloy types containing up to about 5% nickel, 2% chromium and not

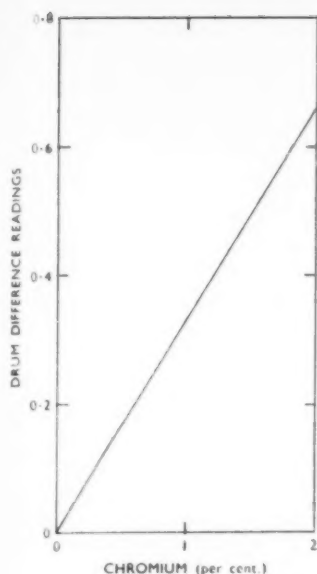


Fig. 1.—Calibration curve for chromium.

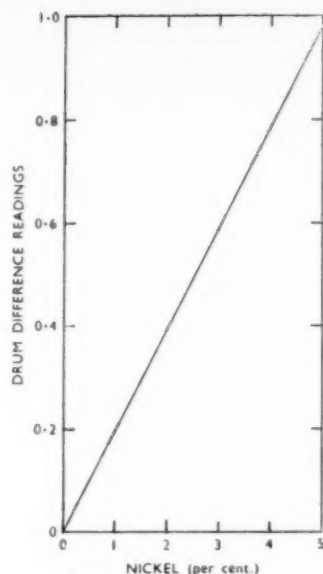


Fig. 2.—Calibration curve for nickel.

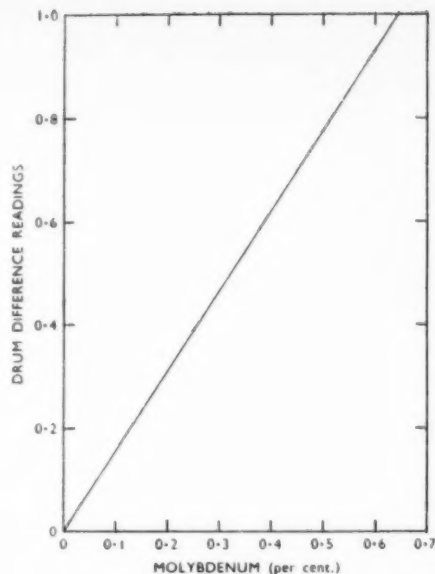


Fig. 3.—Calibration curve for molybdenum.

over 1% molybdenum. Higher-alloy types would, of course, require other dilutions and, preferably, special calibration. The procedure finally standardised for the former class is typical, and is described below.

Typical Procedure

A 1 g. sample of the steel is taken up in 40 ml. Spekker acid, oxidised with a few drops of nitric acid and fumed to destroy carbide, if any should remain. The fuming should be continued to eliminate the excess nitric acid in any case, since this reagent interferes in the molybdenum determination. In the case of some of the higher-alloy materials, a little hydrochloric acid added prior to fuming assists solution, and is, of course, likewise eliminated at fuming. This operation is best conducted in a 350 ml. Erlenmeyer flask, to avoid excessive loss of acid and facilitate the subsequent cooling. When solution is complete, the contents of the flask should be diluted to about 100 ml., and allowed to boil steadily. A saturated solution of potassium permanganate is now added dropwise to a permanent pink colour and the boiling continued for a few minutes, adding more permanganate, as required, to maintain a clear pink colour. Finally, two Analoid pellets (0.75 g. each) of ammonium persulphate are added and, when the action has subsided, three or four drops of strong hydrochloric acid. If chromium is present, the solution comes up to a clear orange-yellow. After further boiling for a minute or so, the flask is cooled and the solution made up to 200 ml. in a standard flask. The chromium can now be measured directly in the absorptiometer, using 2 cm. cells and the violet No. 601 filter, water-water setting 1.0. Pure iron, treated in the same way, is used as a "blank" and the difference reading read off the previously calibrated graph. Fig. 1 shows the graph obtained using the mercury-vapour lamp.

To obtain a suitable dilution for the estimation of nickel, 100 ml. of the above solution is taken off (0.5 g.), and made up to 250 ml. in a standard flask. From this,

10 ml. is pipetted off for colour and "blank." This is treated in the ordinary way with ammoniacal glyoxime and iodine to develop the brownish-red colour of nickel, diluted to 100 ml. and difference readings taken. Using a 1 cm. cell and green No. 604 filters, the graph shown in Fig. 2 was constructed from known standard nickel solutions. Again this is linear, passing through the origin.

For the estimation of molybdenum, the solutions employed were designed to improve the stability of the colour produced by stannous chloride-sulphocyanide reagents. The acid concentration is kept high by the use of 50% sulphuric acid and, as previously mentioned, an addition of bromide in the form of 10% solution of potassium bromide is also made. Under these conditions, the red iron colour bleaches out rapidly, leaving a stable brown molybdenum colour which can be measured in as little as five minutes standing time. This itself is an advance on the normal procedure, where at least 20 minutes are required to complete the fading of the iron colour. The procedure finally adopted is as follows: two 20 ml. portions of the steel solution are pipetted into 100 ml. flasks, and the following reagents added successively; 10 ml. each, 50% sulphuric acid, 10% potassium bromide, 10% potassium thiocyanate, and 10% stannous chloride containing 5% hydrochloric acid, and the whole made up to 100 ml. The blank contains all the reagents with the exception of the potassium thiocyanate, and after standing at least five minutes, the difference reading is measured. Standards treated in this way gave a straight line passing through the origin, as illustrated in Fig. 3. Since the colour is rather pale, 4 cm. cells are used with the green No. 604 filter.

The advantages of the foregoing methods are a considerable increase in speed and a substantial lowering of cost when compared with other methods. Apart from the elimination altogether of the costly and even dangerous perchloric acid, the saving in silver nitrate can be quite impressive. The reagents used in the new

Comparative Acid Costs

Perehloric Acid	£2/5	—
Spekker Acid	—	4/-
Persulphate Tabloids	—	1/-
Potassium Permanganate, Hydrochloric Acid, etc. (say)	—	1/-
	£2/5	6/-

method are all common everyday chemicals, and as will readily be seen, are without exception quite inexpensive. An estimate of the relative costs for 250 estimations of nickel, chromium and molybdenum by the perchloric

acid and "Spekker" acid method is set out here on the basis of 40 ml. "Spekker" acid against 20 ml. perchloric acid, per estimation: these are the usual amounts employed in the two methods.

Aside altogether from the financial advantage of the new method, there is a worthwhile increase in speed and, because of the absence of heavy fumes, a decided improvement in the atmosphere of the laboratory.

Acknowledgment

Acknowledgment is made to the Directors of Albion Motors, Ltd., Glasgow, for permission to publish this information.

Exhibits of Metallurgical Interest at the Physical Society Exhibition

The exhibits at the Physical Society's annual exhibition of scientific instruments usually include a number of interest to workers in the metallurgical field. The last was no exception and in this issue we conclude a short series of reviews in which such items have been described.

Thickness Measurement

THERE are many instances where thickness measurements are desirable, and where it is impossible to use the ordinary calipers and micrometers for the purpose. A number of instruments based on ultrasonics and on radiation absorption and scatter has been developed recently and several were displayed at the exhibition.

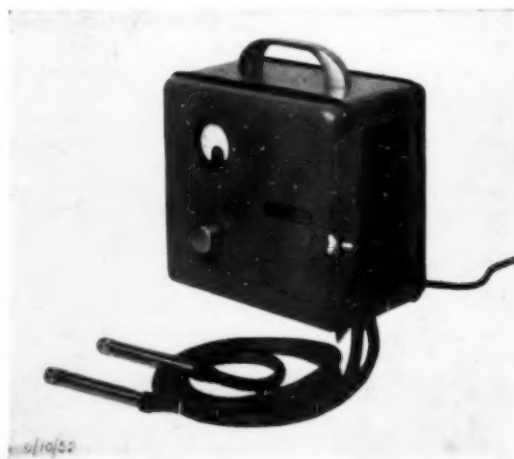
One of those based on ultrasonics is the Kelvin Hughes depth gauge which is a small addition to the standard flaw detector. This instrument was developed for checking the thickness of pipe and plate which might have been corroded or eroded in service. The reference unit consists of a column filled with a liquid in which are immersed two quartz crystals, one transmitting and one receiving. The time for a pulse of ultrasonic energy to travel from one crystal to the other in the liquid is known, and the distance between the crystals can be altered to increase or decrease this travel time. Traces from such a unit can be adjusted so that they are superimposed on the trace set up by the metal being measured, and the metal thickness can then be read instantly. This form of gauge makes the measurement independent of current supply variation and other variables, and enables faults in the equipment to be shown up at once.

The Dawe Visigage is also based on ultrasonics. A quartz crystal sets up ultrasonic vibrations normal to the surface of the material. The crystal is excited by an electronic oscillator, the frequency being represented by distance along the time base trace of a C.R.O. As the frequency passes through the fundamental or a harmonic resonance value of the material under test, increased power is drawn from the oscillator. The power change is amplified and used to provide a vertical pip on the calibrated time base trace.

The principle of the gamma backscatter gauge shown by Ekco Electronics, Ltd., is that when gamma rays pass through steel a proportion will be deflected by Compton scattering of which some will be scattered through 180°. During this process they will lose energy to the extent of twice the Compton wavelength. If Cobalt 60 is used as

a source, the backscattered radiation will return at about 200 keV. By means of a differential discriminator circuit the reflected protons are selected from the primary radiation and fed into a counter rate-meter circuit. The unit has built into it an E.H.T. supply for the photo-multiplier tube and suitable time constants to remove random fluctuations on the indicating meter. Also shown by Ekco were a nucleonic thickness gauge with automatic standardisation and scanning; a scanner intended for use with the automatic thickness gauge on applications not requiring all the facilities of the much larger standard scanner; and a nucleonic thickness gauge suitable for either transmission or backscatter techniques, using a vibrating reed method of signal application.

A prototype gamma backscatter thickness gauge for measuring the thickness of metals where only one side is accessible was shown by the Baldwin Instrument Co.,



Solus-Schall portable magnetiser

Ltd. A production unit seen on the same stand uses the transmission of gamma rays to measure the thickness of sheet metal during hot rolling. This gauge employs a scintillation detector and provides distinct readings at short time intervals. Each reading represents the mean thickness of the strips during the preceding interval. The result is displayed on a lamp board and gives a visual representation of the longitudinal profile of each strip. Automatic standardisation whilst no strip is passing through the measuring head is incorporated. One version of this instrument has been used for gauging the wall thickness of hot steel tubes.

Reference has been made in recent issues of *Metallurgia* to the plating thickness tester developed by the British Non-Ferrous Metals Research Association. This instrument is now being developed by Elliott Brothers (London), Ltd., as a commercial proposition. It operates by measurement of the current driven through the plating material by a thermal e.m.f. developed between the base metal and the plating at a selected point. This current is amplified in a high-stability D.C. magnetic amplifier

with second harmonic modulator input stage, and is displayed on an indicator or recorder, or is employed to operate a relay for comparison testing purposes.

Portable Magnetic Crack Detector

The basic principles of the magnetic powder method of crack detection are now well-established, the main variations in procedure concerning the method of magnetisation, the method of applying the fluid, and the method of inspection, etc. The portable magnetiser shown by Solus-Schall, Ltd., uses the method of passing heavy electric currents through or around the specimens. It incorporates a transformer to give a heavy current of some 750 amps., which can be passed into the specimen by a pair of metal electrodes, or the secondary leads can be coiled round it and short-circuited. The flash-loop model also incorporates a ten-core cable with the turns series-linked, which can be coiled round the specimen and connected direct to the mains through a fuse. The short-circuit is high, giving adequate ampere-turns for magnetisation. This method can be used with D.C. supplies, since the transformer is not utilised.

Cambridge Polarographic Research Laboratory

THE growing demand for the services of specialists in the various fields of science and technology to-day, together with the present acute shortage of trained and experienced scientists, is creating a problem of considerable magnitude in the realm of chemistry, where, in spite of the development of physico-chemical analytical instruments as time-saving aids in the laboratory and on the plant, there is still an unsatisfied demand for chemists skilled in the operation of these instruments, and in the interpretation of data. This is no less true in the highly specialised field of polarography where the present shortage of semi-skilled and skilled polarographers is preventing the benefits of this technique from being freely available to science and industry. In some countries this shortage of polarographers has been met by the formation of groups of experts whose services to science and industry are available thus to ensure that the benefits arising from the use of this technique are available to all.

The earliest example of this type of specialist organisation was the Central Polarographic Institute of Czechoslovakia established in Prague by Professor J. Heyrovsky, who invented the polarograph in 1925. This Institute is noted for its pioneering work in developing the theory of polarography and applying this knowledge generally to the problems of medicine and science. A Central Institute for the Study of Polarography has been set up at Padova in Italy under Semerano; other groups of polarographers are established in Denmark, Sweden, India and Japan, and a great deal of work of importance in the metallurgical and engineering fields has been carried out. Thus a number of countries throughout the world have established their groups of experts in this field, and have made valuable contributions to scientific investigations and to analytical chemistry.

In Great Britain no exclusive outstanding experimental and development organisation has been created, although many small units have been doing valuable work in this field. The Cambridge Instrument Co., Ltd.,

was one of the first, if not the very first, maker of polarographs in this country, the earliest instruments being sent out just before the second world war. Dr. G. Jessop of the Research Department of the Company has done a large amount of work on the development of polarographic instruments and techniques. Further, the Research Department has always endeavoured to help users of polarographs in the solution of their own particular problems. The volume of such work has so increased that it has not been possible, without delaying more fundamental research, to give the immediate service which is very desirable with such problems.

To remove this difficulty, and to enable the company to develop its polarographic equipment more rapidly, a special Polarographic Research Laboratory was recently opened by Professor J. Heyrovsky, and will be in the charge of Mr. W. J. Parker, B.Sc., A.R.I.C., A.M.Inst.F. The opening ceremony, under the chairmanship of Sir J. A. N. Barlow, Bt., G.C.B., K.B.E., was attended by a representative gathering from the academic, research and industrial fields. This laboratory, which will be employed exclusively on polarographic problems and development, is adjacent to the Company's Cambridge Works, and the work carried on there will be carefully co-ordinated with the programme of work which will continue in the main Research Department. The specialised services of the laboratory will be available for advice and help to firms and to research workers interested in this subject, and it will be fully equipped for the demonstration of polarographic instruments and techniques.

Castings for Coil Unloaders

Two new coil unloader carriage assemblies being built by Davy-United Engineering Co., Ltd., for the Abbey Works of The Steel Company of Wales, Ltd., have tilting frame base castings, 7 ft. 6 in. \times 2 ft., weighing 65 cwt., supplied by Edgar Allen & Co., Ltd.

A Simple Device for Plotting Inverse-Rate Cooling Curves

By

L. H. Cope, A.I.M., A.M.Inst.W., F.R.N.S.
and F. Kellett

Corby Technical College

WHEN observing transformations in the solid state the small heat evolution and the sluggish nature of many of the changes necessitates the use, not of simple time-temperature curves, but of "inverse-rate" cooling curves. In practice this involves plotting a graph on which is shown the time taken for successive decrements in temperature. For accurate work: (a) the temperature intervals must be small, and (b) each interval must be individually timed. The former problem is solved satisfactorily by the use of a mirror galvanometer and lamp-scale unit in conjunction with a potentiometer. Since the earliest work on thermal analysis, devices of varying degrees of complexity have been invented to overcome the latter.^{1, 2, 3.}

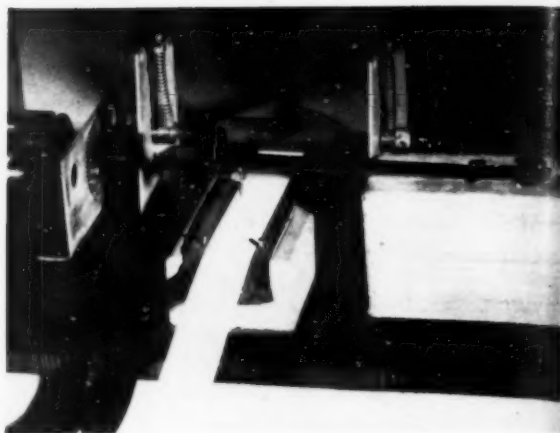
Probably the simplest way is to use stop watches; attempting to start one coincident with stopping the other, but the method is tedious, mistakes arise and it is almost impossible for one person to make notes at the same time.

Inexpensive Equipment

The present apparatus has been devised as a simple inexpensive piece of equipment whereby one observer can record his results without tedium or loss of accuracy. From the photograph it can be seen that it is constructed largely from laboratory junk. It consists of a pair of rubber rolls driven at a constant speed to pull forward a strip of paper over a platen faced with rubber. Above the platen is mounted a thin spring strip fitted with a push button and a gramophone needle. The button is quickly depressed at appropriate moments to record the passage of the galvanometer light spot over a division on the scale unit. There is usually ample time to note the e.m.f. on the paper strip, say every five intervals as a reference for checking the plot later. Time intervals can then be taken directly from the paper roll by means of dividers and a graph plotted more easily and surely than from a list of figures. The human factor in the experimental work is largely eliminated and the paper roll serves as a complete record of the experiment should any query arise later.

Constructional Details

It is important that the speed should be variable, to meet different experimental conditions, yet constant for the duration of a test when once set. These conditions were obtained from a small series-wound electric motor



fed from a continuously variable auto-transformer. Reduction gearing assembled from standard constructional toy parts gave a ratio of 1,400 : 1 which provided ample torque and a positive drive at speeds ranging from 0.5 to 9 in./min. This was found adequate for most purposes.

The rolls were made by pushing short lengths of rubber pressure tubing onto steel rods coated with adhesive. The upper roll was lightly spring loaded to ensure no-slip conditions on the paper feed.

The "chart" does not need to be more than $\frac{3}{4}$ in. wide. Gummed brown paper is quite satisfactory and has the advantage of being cheap and easily obtained. "Ticker" tape can also be used but may be a little too narrow for reference figures to be written upon it. To prevent any tendency for side movement to occur four guide pins were driven into the platen; two on each side of the paper strip.

Investment Casting Agreements

SHAW PROCESSES, LTD., of 25, Clyde Vale, Dartmouth Road, Forest Hill, London, and 41, Carlisle Street, Newcastle-upon-Tyne, announce that they have recently concluded arrangements with Metropolitan-Vickers Electrical Co., Ltd., whereby Shaw Processes, Ltd., now have the exclusive right to arrange sub-licence agreements relative to the Investment X process of precision casting, which was described in a paper by Mr. J. S. Turnbull presented before the Institution of Mechanical Engineers in London on December 31st, 1954. The Investment X process is basically a lost wax process, but effects very considerable simplification and economies in that process, and is applicable to castings of much larger size than it is normally possible to make by lost wax methods. The process is protected by patents, both issued and pending, throughout the world, and is available as a fully proven process which is in constant production use.

Shaw Processes, Ltd., have now concluded an agreement with British Industries Corporation of New York, for the immediate establishment of a Company to be named the Shaw Processes Development Corporation Inc. which will establish demonstration plant and a laboratory at Long Island, and will exploit the Shaw process of precision casting by the granting of licences throughout the United States and Canada.

